U-Mo Fast Reactor Fuels: Microstructure Characterization and Fuel Clad Chemical Interaction

By Sibasis Chakraborty

(ENGG01201204014)

BHABHA ATOMIC RESEARCH CENTRE, Mumbai

A thesis submitted to the Board of Studies in Engineering Sciences In partial fulfilment of requirements for the Degree of

DOCTOR OF PHILOSOPHY of HOMI BHABHA NATIONAL INSTITUTE



September 2019 Homi Bhabha National Institute

Homi Bhabha National Institute

Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by **SIBASIS CHAKRABORTY** entitled "**U-Mo Fast Reactor Fuels: Microstructure Characterization and Fuel Clad Chemical Interaction**" and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

1 2		11.	
Chairman	Dr. Vivekanand Kair	n Mar	Date: 11 9 19
Guide / Convener	Dr. Renu Agarwal	Renn Ag al	Date: 11 9 19
External Examiner	Dr. Indranil Manna	Indraw (do	- Date: 1.8.19
		ρ	
Member1	Dr. R. Tewari	hard	Date: 11/09/19
Member2	Dr. Alok Awasthi	AlokAwasthi	Date: 11/9/2019
Member3	Dr. J. B. Singh	prices.	Date: 12/09/2019

Final approval and acceptance of this thesis is contingent upon the candidate's submission of the final copies of the thesis to HBNI.

I/We hereby certify that I/we have read this thesis prepared under my/our direction and recommend that it may be accepted as fulfilling the thesis requirement.

Date: 11/9/19 Place: Tromboy

Rem Ag 1

Signature Guide

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at Homi Bhabha National Institute (HBNI) and is deposited in the Library to be made available to borrowers under rules of the HBNI.

Brief quotations from this dissertation may be permitted without special permission. But accurate acknowledgements of source is to be mentioned. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the Competent Authority of HBNI when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other cases, however, permissions must be obtained from the author.

Date:1/10/19

Sibaris Chakrabotts

<Sibasis Chakraborty>

Declaration

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

Siban's Chakraboth

Date:1/10/19

<Sibasis chakraborty>

List of publications arising from the thesis

- 1. Micro-structural study and Rietveld analysis of fast reactor fuels: U-Mo fuels, Journal of Nuclear Materials 467 (2015) 618-627
- Microstructure characterization and phase field analysis of dendritic crystal growth of y-U and BCC-Mo dendrite in U-33 at.% Mo fast reactor fuel, Journal of Material Research, Volume 33, Issue 2, 29 January 2018, pp. 225-238.
- 3. Fuel Clad Chemical Interaction of U-Mo Fast Reactor Fuel, Journal of Nuclear Materials 516 (2019) 1-10.

Date:1/10/19

Siban's Chakraboth

<Sibasis Chakraborty>

Paper & Poster Presented in Conferences

 "Phase Field Model of U-Mo alloy Solidification"; Sibasis Chakraborty, Gargi Choudhuri, J. Banerjee, P. S. Somayajulu, Renu Agarwal, K.B. Khan, Arun Kumar, MMMD 2014, Mumbai, India.
 "Thermal Investigations and Microstructural study of U-Mo alloy"

S.Chakraborty, G.Choudhuri, J.Banerjee, Renu Agarwal, K.B.Khan,

P.S.Somayajulu, Arun Kumar, MRSI 2012, Mumbai, India.

Siban's Chakraboth

Date:1/10/19

< Sibasis Chakraborty >

Dedicated to Maa, Babai and didi

Acknowledgement

I would like to express my deep and sincere gratitude to Dr. Srikumar Banerjee, Chancellor, HBNI for his constant support and encouragement during this thesis work. I would like to express my sincere gratitude to my Guide Dr. Renu Agarwal for her guidance, and all-round support that led to the successful completion of this work. I would like to express my sincere appreciation to my technical advisor Shri Arun Kumar for having many fruitful technical discussion. I would like to thank Dr. Jaydipta Banerjee, for his kind and prompt cooperation in carrying out experimental work in the laboratory. I would like to thank my wife and co-author Dr. Gargi Choudhuri. This work would have not been possible without her love and support in every aspect of it. I would also like to thank all the members of the doctoral committee for their valuable suggestions and support throughout the duration of work.

I would like to thank Dr. P.S.Somayajulu and Shri Vivek Bhasin for their support and valuable technical discussion.

I would like to extend special thanks to all my fellow members of Radiometallurgy Division and Nuclear Fuels Group for providing assistance and support whenever I needed them.

Siban's Chakraboth

Date:1/10/19

< Sibasis Chakraborty >

Contents

	Summary		i
	List of Figure	es	xiii
	List of Table	S	xxi
List	List of Abbreviation		xxii
	Chapter 1: Introduction		1
	1.1	Background	1
	1.2	Motivation	4
	1.3	Objective of the work	5
	1.4	Organization of thesis	7
	1.5	References	8
Chapter 2: Literature Review		9	
	2.1	Pure Elements: Uranium, Plutonium, Molybdenum, Zirconium	10
	2.2	Alloying elements of U based alloys:	11
		2.2.1 U-Zr and U-Pu-Zr	11
		2.2.2 U-Mo and U-Pu-Mo	16
	2.3	Fuel clad mechanical and chemical interaction (FCCI) in	
		metallic fuel	20
	2.4	References	23
	Chapter 3: M	laterials and Methodology	26
	3.1	Material	26
	3.2	Arc melting furnace	26

3.3	Thermal treatment	27
3.4	Fabrication of Diffusion couples and thermal treatment	28
3.5	Optical Microscope	31
3.6	Scanning Electron Microscopy with EDS analysis	31
3.7	Electron Backscattered Diffraction (EBSD)	33
3.8	Micro-hardness measurement	35
3.9	X-Ray powder diffraction and Rietveld analysis	36
3.10	References	37

Chapter 4: Micro-structural study and Rietveld analysis of fast reactor fuels:

U·	Mo fue	ls	39
4.1	Micro	ostructure and phase analysis of as-cast alloys	43
	4.1.1	U-2 at.% Mo alloy & U-5 at.% Mo alloy	45
	4.1.2	U-10 at.% Mo alloy	46
	4.1.3	U-33 at.% Mo alloy	49
	4.1.4	EBSD analysis of U-33 at.% Mo cast alloy for segregation	54
4.2	Micro	ostructure and phase analysis of annealed alloys	56
	4.2.1	U-2 at.% Mo alloy & U-5 at.% Mo alloy	56
	4.2.2	U-10 at.% Mo alloy	58
	4.2.3	U-33 at.% Mo alloy	60
4.3	Micro	p-hardness of U-Mo alloys	62
4.4	Summ	ary	64
4.5	Refere	ences	66

Chapter 5: Development of PFM to predict microstructure evolution in			
U-	Mo alloy during solidification	69	
5.1	Phase Field model for Solidification	70	
	5.1.1 Entropy Functional	70	
	5.1.2 Evolution Equations	71	
	5.1.3 Anisotropy in Interfacial Energy & attachment coefficient	77	
	5.1.4 Finite element method & Initial microstructure	78	
5.2	(Mo)-dendrite Microstructure characterization and PFM simulation	n 81	
	5.2.1 Evolution of Mo-dendrite & Validation through EDS		
	analysis	82	
	5.2.2 Tip-velocity of (Mo)-dendrite	86	
	5.2.3 Variation of tip velocity with undercooling	87	
	5.2.4 Temperature profile of Mo dendrite during crystal growth	88	
5.3 γ-	-(U)-dendrite Microstructure characterization and PFM simulation	89	
	5.3.1 Evolution of (γ) -dendrite & Validation through EDS		
	analysis	90	
	5.3.2 Tip-velocity of (γ) -dendrite	93	
	5.3.3 Variation of tip velocity with undercooling	94	
	5.3.4 Temperature profile of γ dendrite during crystal growth	95	
5.4	Summary	97	
5.5	References	98	

Chapter	6: Fu	el Clad Chemical Interaction of U-Mo Fast Reactor Fuel	102
	6.1	Diffusion Couple Experiments	103
		6.1.1 At 650°C/14 days, 30 days and 85 days	106
		6.1.2 At 675° C/ 7 days, 14 days and 40 days	114
		6.1.3 At 700° C/ 3 days, 7 days and 15 days	115
	6.2	Discussions	122
		6.2.1 Clad wastage zone	123
		6.2.2 Slug Penetration Zone	126
		6.2.3 Diffusion path in ternary U-Mo-Fe	127
		6.2.4 Calculation of growth constant	128
	6.3	Summary	133
	6.4	References	134
Chapter	7: Co	onclusions & Scope for further research	137
7	. 1	Conclusions	137

141

Scope for further research

7.2

Summary

Uranium molybdenum fuel is a candidate material for both fast and thermal reactors. Pure uranium has three stable allotropic phases, orthorhombic α -U (-231 °C to 667.3 °C, 4 atoms/ cell), tetragonal β -U (667.3 °C to 774.8 °C, 30 atoms/cell) and body-centered cubic γ -U (774.8 °C to 1135 °C, 2 atoms/cell). Other than BCC y-U, all allotropes of uranium, orthorhombic (α -U) and tetragonal (β -U), show anisotropic coefficients of thermal expansion. The phase diagram of U-Mo shows that the cubic phase is isotropic, it provides the advantage of isotropic expansion and uniform thermo-physical property along different crystallographic directions. The cubic BCC phase also has the advantage of higher solubility of alloying elements, which minimizes fuel constituents' migration. Higher melting point of the fuel ensures higher safety margin for fuel melting during the off-normal condition. Molybdenum has a BCC crystal structure up to its melting point, at 2623 °C. It has high thermal conductivity and can be added to stabilize the γ -U phase over a wider temperature range while maintaining a high uranium density. 'Mo' has reasonable solubility in γ -U and forms γ -(U,Mo), which shows isotropic expansion with increase in temperature. With increasing Mo content, the melting point, gamma stability and swelling resistance of the U-Mo alloy fuel, are found to increase. High melting point and thermal conductivity along with low stored heat of the fuel ensure higher safety margin for fuel during the off-normal condition.

1. **Microstructure Characterization of U-Mo Alloys**: U-Mo fast reactor fuel is fabricated through injection-casting route. The microstructure of as-fabricated fuel is similar to that of as-cast alloy formed by arc-melting. This as-fabricated fuel tends to undergo transition to equilibrium phases soon after irradiation. In the present work, equilibrium phases of the alloys were generated by homogenization annealing. Thorough understanding and characterization of as-cast and annealed microstructures were the main objectives of this thesis. To fulfill that objective, different U-Mo alloys (2, 5, 10 and 33 at.% Mo) in as-cast and annealed conditions, were characterized by X-ray diffraction and Rietveld analysis, optical microscope, scanning electron microscope and energy dispersive spectrometry (EDS). Electron back scattered diffraction (EBSD) analysis of as-cast U-33 at.% Mo-alloy was done for studying preferred orientations and segregation patterns in the microstructure.

2. Phase-Field Modeling of U-33 at.% Mo: During microstructural investigations of cast U-Mo alloys, two types of dendrites were found in as-cast alloys containing 33 at.% Mo. To understand the phenomenon involved in this process, Phase-Field model for solidification was developed. This model could predict the microstructure and segregation pattern during solidification of the alloy. These computational results were compared with experimental results and this helped in understanding importance of different phenomena taking place during solidification, at different under-cooling.

3. Fuel-Clad Chemical Compatibility of U-33 at.% Mo with T91: One of the detrimental factors of metallic fuels in fast breeder reactor is fuel-clad chemical interaction (FCCI), due to interaction of U and Fe. This fuel-clad chemical interaction should be avoided or minimized to increase fuel burn-up. The main reason behind FCCI is the formation of low melting eutectic between U and Fe at temperature 725 °C, (liquid = $UFe_2 + UFe_6$). This reaction degrades the mechanical property of the clad and causes clad failure. To address this issue in U-Mo fuel, fuel-clad chemical compatibility tests were carried out with high Mo content (33 at.% Mo) alloy and T-91 cladding material. The U-33Mo/T91 formed an autogenerated Mo-rich layer in fuel clad interface and significantly reduce U and Fe diffusion compared to other diffusion couples like U-23Zr/T91.

Due to its excellent thermo-physical property, negative temperature coefficient of reactivity, low stored heat and excellent fuel clad interaction behaviour and absence of Zr water reaction, U-Mo fuel cladded with T91 can act as an accident tolerant fuel in advanced fast and thermal reactors.

List of Figures

Fig. 1.1	Sodium cooled pool type fast reactor.	1
Fig. 2. 1	U–Zr binary phase diagram.	12
Fig. 2. 2	Pu-Zr binary phase diagram.	12
Fig. 2.3	Cross-sectional photomicrograph of the post-irradiated fuel along	16
	with EPMA scan of U, Zr and Pu.	10
Fig. 2.4	U-Mo binary phase diagram.	17
Fig. 2.5	Pu-Mo binary phase diagram.	17
Fig. 2.6	U-19Pu-10Zr pseudo-binary phase diagram . The vertical broken	
	line indicates the phase field of U-19Pu-10Mo in typical reactor	19
	operations.	
Fig. 2.7	Isopleth of U/Pu = 3. The vertical broken line indicates the phase of	20
	U-19Pu-10Mo in typical reactor operations.	20
Fig. 2.8	U-Zr-Fe ternary phase diagram [2.24] and diffusion path(dotted gray	
	lines) at 650°C. Open circles indicate approximate average	22
	compositions of the layers.	
Fig. 2.9	Backscattered electron micrographs from U-10 wt.% Zr vs Fe	
	diffusion couple annealed at 650 °C for 400 h [2.24].	22
Fig. 3.1	The vacuum Arc melting unit along with schematic of arc melting	27
	system [3.1]	<i>∠</i> /
Fig. 3.2	U-Mo TTT Diagram [3.2].	28

Fig. 3.3	Glass sealing of diffusion couple.	29
Fig. 3.4	Engineering drawing of the diffusion couple.	30
Fig. 3.5	Cross sectional view of the diffusion couple indicates presence of Ta	
	foil surrounding the T91 to prevent interaction between diffusion	30
	couple and jig.	
Fig. 3.6	Schematic diagram of scanning electron microscope [3.3].	32
		52
Fig. 3.7	Typical pear shaped interaction volume evolves when accelerated	33
	electron strikes the sample in SEM [3.4].	
Fig. 3.8	EBSD configuration inside the SEM chamber [3.5].	35
Fig. 4.1	U-Mo phase Diagram [4.24].	43
Fig. 4.2	Rietveld plot for U-2 at.% Mo in as-cast condition. Dots are	
	experimental scan, solid line is calculated pattern and bottom line is	45
	the residual curve.	
Fig. 4.3	Rietveld plot for U-5at.%Mo as-cast. Dots are experimental scan,	46
	solid line is calculated pattern and bottom line is the residual curve.	70
Fig. 4.4	As cast microstructure of U-10 at.% Mo shows single phase grains	47
	with oxide inclusions.	Τ/
Fig. 4.5	XRD pattern of U-10 at.% Mo as-cast alloy clearly indicates the	18
	splitting of (-131) and (131) lines.	-10
Fig. 4.6	Rietveld plot for U-10 at.% Mo as-cast alloy. Dots are experimental	
	scan, solid line is calculated pattern and bottom line is the residual	48
	curve.	
Fig. 4.7	As -cast microstructure U-33 at.% Mo at low mag. showing dendritic	40
	morphology.	77

Fig. 4.8	Dendritic microstructure observed in U-33 at.% Mo alloy in as-cast	49
	condition at high magnification.	
Fig. 4.9	Higher magnification microstructure of as-cast alloy with 33 at.%	50
	Mo, to view 'Mo' rich dendrites as indicated by number 1 in Fig.4.8.	
Fig. 4.10	EDS spectrum (indicated with number 1 in Fig.4.8) taken on Mo rich	51
	dendrites in as cast U-33 at.% Mo alloy.	
Fig. 4.11	EDS spectrum of enveloping region (indicated with number 4 in Fig.4.8) in as-cast U-33 at.% Mo alloy shows 42.5 at.% 'Mo'.	51
Fig. 4.12	EDS spectrum of 'U' enriched dendrites (indicated with number 2 in Fig.4.8) in as-cast U-33 at.% Mo alloy indicates 34-40 at.% 'Mo'.	52
Fig. 4.13	EDS spectrum of matrix (number 3 in Fig.4.8) in as-cast U-33 at.% Mo alloy shows 24-27 at.% 'Mo'.	52
Fig. 4.14	Rietveld plot for U-33at.%Mo as-cast. Dots are experimental scan,	51
	solid line is calculated pattern and bottom line is the residual curve.	54
Fig. 4.15	Inverse pole figure map (IPF-Z) of as-cast U-33at.%Mo. (The colour	55
	code represents orientation of grains along the z direction).	55
Fig. 4.16	Band Contrast map of as-cast U-33at.%Mo.	55
Fig. 4.17	IPF-Z map superimposed with Band contrast and EDS count of as-	
	cast U-33at.%Mo showing dendritic pattern along with micro-	56
	segregation. The Mo-dendrite is brightest (indicated by no.1), other	50
	dendrites are γ -(U) dendrite (indicated by no. 2).	
Fig. 4.18	Lamellar microstructure with dendrite of oxide was observed under	57
	SEM with dendrites in annealed U-2 at.% Mo alloy.	51
Fig. 4.19	Lamellar microstructure was observed along with oxide inclusions in	57
	annealed U-5 at.% Mo alloy.	51

Fig. 4.20	Rietveld plot for U-5at.%Mo annealed alloys showing only presence	
	of orthorhombic α . Dots are experimental scan, solid line is	58
	calculated pattern and bottom line is the residual plot.	
Fig. 4.21	Lamellar microstructure was observed in annealed U-10 at.% Mo	50
	alloys with increasing second phases.	39
Fig. 4.22	Rietveld plot for U-10at.%Mo annealed alloys showed presence of	
	orthorhombic α and U ₂ Mo. Dots are experimental scan, solid line is	60
	calculated pattern and bottom line is the residual curve.	
Fig.4.23	Single phase microstructure with small oxide inclusions in annealed	61
	U-33 at.% Mo alloy.	01
Fig. 4.24	Rietveld plot for U-33at.%Mo annealed alloys showing presence of	
	$U_2 Mo$. Dots are experimental scan, solid line is calculated pattern	61
	and bottom line is the residual curve.	
Fig. 4.25	Variation of hardness with Mo content (in at.%) in annealed U-Mo	63
	alloys, in Vicker's Scale using 300 gm load.	05
Fig. 5.1	Double well interpolation function $g(\phi)$.	73
Fig. 5.2	Nature of interpolation function $p(\varphi)$, it is zero at $\varphi=0$ and 1 at $\varphi=1$	74
Fig. 5.3	Adaptive meshing at the solid-liquid interface.	79
Fig. 5.4	(a) SEM image of (Mo)-dendrite, (b) EDS layered image having	
	BSE image along with elemental X ray map of U and Mo, (c) & (d)	83
	Elemental X ray mapping image of U and Mo respectively, (e)	05
	Representative EDS profile taken on (Mo)-dendrite.	
Fig. 5.5	(a) Elemental X-ray map superimposed with SEM BSE image of	
	(Mo)-dendrite with at.% Mo concentrations measured by EDS,(b)	85
	Concentration map (mole fraction of Mo) of simulated Mo dendrite	

assuming $D_{U/Mo}=10^{-9}$ and $D_L=10^{-8}$ m²/sec (100 non-dimensional time step) at undercooling 20 K.

Fig. 5.6	Tip-velocity of (Mo)-dendrite at different non-dimensional time.	87
Fig. 5.7	Plot of tip velocity vs. under-cooling for (Mo)-dendrite showing	00
	higher tip velocity at higher under-cooling.	88
Fig. 5.8 (a)	Cut-line drawn through the temperature field of Mo dendrite (The	
	scale bar depicts the temperature in ($^{\circ}$ C)	89
Fig. 5.8 (b)	Plot of temperature profile through cut line of a (Mo)-dendrite at	
	different non-dimensional time of crystal growth.	89
Fig. 5.9	(a) SEM image of γ -dendrite, (b) Elemental X ray image super	
	imposed with BSE image of γ -dendrite, (c) Elemental X ray map of	
	U shows high U enrichment in surrounding matrix, (d) Elemental X	00
	ray map of Mo shows high Mo enrichment at the centre of dendritic	90
	arm in γ -dendrite and (e) Representative EDS profile taken on γ -	
	dendrite.	
Fig. 5.10	(a)-(c) Evolution of concentration field of U-Mo γ -(U) dendrites	
	from pre-nucleated γ -(U) nucleus under non-isothermal condition at	
	100, 200 and 400 non-dimensional time step respectively. The	
	simulation box size was 400x200 in non dimensional space, (d) The	92
	concentration of Mo (at.%) measured in EDS at respective position of	-
	γ -dendrites are given, (e) Evolution of U-Mo γ phase dendrites from	
	pre-nucleated gamma nucleus at 500 non-dimensional time steps	
	under non-isothermal condition.	
Fig. 5.11	Tip-velocity of (γ -U)-dendrite at different non-dimensional time	94

vii

(under-cooling 38 K).

Fig. 5.12	Plot of tip velocity vs. under-cooling for (γ -U)-dendrite showing	05
	higher tip velocity at higher undercooling.	95
Fig. 5.13	Plot of temperature profile through cut line of a γ -(U) dendrite at	
	different non-dimensional times of crystal growth (tip of the curves	96
	represent solid-liquid interface).	
Fig. 6.1	The microstructure in a U-33Mo/T91diffusion couple annealed at	
	700° C for 15 days. Gaps between red thick lines show average	100
	thickness of reaction layers. L1: UFe2+ θ + τ , L2: U6Fe, L3: Mo-	102
	autogenous layer, L4: lamellar Mo+U6Fe.	
Fig. 6.2.	XRD scan after 85 days of heating at 650°C.	105
Fig. 6.3a	The microstructure in a U-33Mo/T91diffusion couple annealed at	107
	650° C for 14 days.	107
Fig. 6.3b	EDS spectrum of bright region in UFe ₂ layer in wt.% after 650°C 14	100
	days annealing	108
Fig. 6.3c	EDS spectrum of dull region of UFe2 layer in wt.% after 650°C 14	100
	days annealing.	108
Fig. 6.3d	EDS profile of Mo rich barrier layer after 650°C 14 days annealing.	109
Fig. 6.3e	Elemental maps of different elements after 650°C 14 days annealing	100
	of the diffusion couple.	109
Fig. 6.3f	Line profile across the interaction layer variation of composition	110
	across the different region after 650°C 14 days annealing.	110
Fig. 6.3g	EDS profile of the bright region (U ₆ Fe) in the pellet side after 650° C	110
	14 days annealing.	110
Fig. 6.3h	EDS profile of dull phase in pellet side after 650°C 14 days	111

annealing.

Fig. 6.3i	EDS profile of U-33 at.% Mo.	111
Fig. 6.4a	BSE of interaction layer formed after 85 days annealing at 650°C.	112
Fig. 6.4b	BSE image and EDS analysis of interaction layer after 85 days	
	annealing at 650°C.	115
Fig. 6.4c	EDS layered image showing elemental mapping 85 days annealing at	112
	650°C.	115
Fig. 6.4d	EDS spectrum of layer 3 after 650°C 85 days annealing.	114
Fig. 6.5	The interaction layer formed at 675°C after 40 days annealing.	115
Fig. 6.6	Lamellar region formed in pellet after 3 days annealing at 700°C.	116
Fig. 6.7a	BSE image showing the position where EDS profile taken in the	117
	interaction layer after 7 days annealing at 700°C.	11/
Fig. 6.7b	EDS profile of Mo rich barrier layer after annealing at 700°C for 7	117
	days.	11/
Fig. 6.7c	EDS profile taken on U_6Fe after annealing at 700°C for 7 days. (U	110
	83.30at.%, Mo 1.61 at.%, Fe 14.64 at.%, Cr 0.46 at.%).	110
Fig. 6.7d	EDS profile of Mo rich lamellar region after annealing at 700°C for 7	110
	days.	110
Fig. 6.8a	BSE image of interaction layer after annealing at 700°C for 15 days.	119
Fig. 6.8b	Elemental maps of elements after 700°C 15 days annealing of the	120
	diffusion couple.	120
Fig. 6.8c	EDS profile of Mo rich region in the lamellar structure after	121
	annealing at 700°C for 15 days.	121
Fig. 6.8d	XRD scan after 700°C 15 days annealing of the diffusion couple.	121

Fig. 6.8e	EDS profile of τ phase within L1 layer , after annealing at 700°C for	100
	15 days.	122
Fig. 6.9	Calculated phase diagram of U-Mo-Fe and calculated diffusion path.	
	A: Fe Clad, B: U ₃₉ -(Fe,Cr) ₅₉ -Mo ₁ , C: U ₂ -(Fe,Cr) ₂ -Mo ₉₆ , D: U ₆ Fe, E:	128
	Slug (U-33 at.% Mo).	
Fig. 6.10	Thickness ² vs time plot at three different temperatures for growth	
	study of clad wastage layer (L1+L2), slug penetration layer (L3+L4)	129
	and Mo (L3) layer.	
Fig. 6.11	The comparison of total growth rate between U-33Mo/T91 and other	
	authors. It clearly showing U-33Mo/T91 has much lower growth rate	122
	than other diffusion couples.	155

List of Tables

Table 2.1	History of fast reactor.					
Table 3.1	Heat treatment of U-Mo alloys.					
Table 3.2	Space group, Wyckoff notation, atomic position and					
	lattice parameter of different phases used during Rietveld					
	analysis.					
Table.4.1	Literature data on metallurgical investigations of U-Mo					
	alloy along with their compositions and type of heat					
	treatments.					
Table 4.2	Lattice parameters obtained from Rietveld Analysis	64				
	using MAUD program.					
Table 5.1	Material parameters for the U-Mo system for simulation	80				
	of γ and Mo rich dendrite					
Table 5.2	EDS analysis of (Mo)- dendrite (at.%).	84				
Table 6.1	Thickness of different layers after annealing at different	105				
	duration and phases present in the reaction layers.					
Table 6.2	EDS analysis of U-33Mo/T91 diffusion couples (at.%).	107				
Table 6.3	The comparison between U-23Zr/Fe-12Cr and U-	123				
	33Mo/T91 interaction layer formation at 700 °C.					
Table 6.4	Diffusivity Parameters obtained from literature.					
Table 6.5	The growth constant (m^2 /sec) calculated at three	131				
	different temperatures for UFe2 and U6Fe layers for					
	calculation of activation energy					
Table 6.6	The total interaction layer growth of different diffusion	132				
	couples					

List of Abbreviations

EBSD	Electron back scattered diffraction
EDS	Energy dispersive spectroscopy
FBR	First Breeder Reactor
FEM	Finite element method
PDE	Partial Differential Equation
PFM	Phase field model
PHWR	Pressurized heavy water reactor
PWR	Pressurized water reactor
SEM	Scanning electron microscopy
XRD	X ray diffraction

Chapter 1: Introduction

'The people who will develop Liquid Metal based Fast Reactor technology will lead the world in the future' -Enrico Fermi [1.1].

1.1 Background

Efficient and sustainable nuclear technology needs to be developed to counter two biggest threats to mankind, which are global warming and poverty. The Generation IV nuclear reactors are being designed to achieve this goal. The generation IV reactors consist of thermal reactors and fast reactors. The thermal reactors considered are: (1) Very-high-temperature reactor (VHTR), (2) Molten-salt reactor (MSR), (3) Supercritical-water-cooled reactor (SCWR). The fast reactors are (1) Gas-cooled fast reactor (GFR), (2) Sodium-cooled fast reactor (SFR) and (3) Lead-cooled fast reactor (LFR). The efficient and high burn-up fast reactors are one of the important cog to achieve this mission.



Fig.1.1 Sodium cooled pool type fast reactor [1.2].

The SFR is one of the most advanced and developed reactor technology. The SFR operates on fast neutron (E:>1 MeV) . The fuel for SFR can be mixed oxide or metallic.

There are two types of SFR designs depending on the heat transfer system, (i) loop type SFR and (ii) pool type SFR (Fig. 1.1). After being heated in the core, within the reactor vessel, the sodium flows to an intermediate heat exchanger before returning to the reactor vessel. In a pool type design the intermediate heat exchanger is internal to the reactor vessel [1.2]. The main feature of the pool type design is that all primary systems are submerged in a pool [1.2]. In loop type design the heat exchanger and pumps of the primary circuit is placed outside the reactor vessel.

In SFR technology the oxide or metallic fuel is cooled by liquid metals like sodium, lead which has high heat transfer property than water. The oxide pellet or metallic slug is encapsulated in ferritic/austenitic stainless steel. The oxide fuel is not compatible with liquid sodium, however, the metallic fuel is compatible with liquid sodium and can be operated safely even in case of small breaches. The nuclear fuel cycle in fast rector is closed fuel cycle and oxide fuel goes for aqueous reprocessing, whereas, metallic fuel is recycled via pyrometallurgical reprocessing. For both types of fuels, the outlet liquid sodium coolant temperature is approximately 500-550 °C. The heat transfer characteristics of metallic fuel is more efficient, because of better heat transfer property of metals over ceramic oxide. This makes all metallic fuelled fast reactors more efficient than oxide fuel as metal alloys have higher thermal conductivity and higher metal atom density. The reliability of the fuel improves when the life-limiting factors like fuel clad interaction, swelling etc. are controlled. The U-Mo alloy had been used as fuel for early metallic fuel fast reactors viz. Enrico Fermi Reactor (Fermi-I) in the USA. A significant number of metallic fuel rods of U-Zr, U-fissium and U-Zr-X have been burnt in EBR and FFTF [1.3]. The world over people has opted for more technologically mature, oxide fuel option. The rationales for extensive usage of oxide fuels are 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 a high breeding ratio, high thermal conductivity and better in-reactor behaviour during transient conditions. The economic competence of metallic fuel driven fast breeder reactor depends on high burnup of metallic fuels. Though currently India is in a process of commissioning Prototype Fast Breeder Reactor (PFBR), fuelled by conventional (U,Pu)O₂ - MOX fuel, but upcoming FBRs are planned to be fuelled by uranium based metallic alloys.

Pure uranium has three stable allotropic phases, orthorhombic α -U, tetragonal β -U and body-centre cubic γ -U. 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 desirable as these elements can raise the fuel solidus temperature and stabilize BCC γ -U phase to lower temperature, thus enhancing its dimensional stability. Fissium is a group of transition elements which are formed during fission of metallic fuel and it is retained in the fuel during reprocessing as it enhances stability of the γ -U phase and solidus temperature of the fuel. The composition of the fissium is reactor based and is generally 2.4 wt.% Mo, 1.9 wt.% Ru, 0.3 wt.% Rh, 0.2 wt.% Pd, 0.1 wt.% Zr, 0.01 wt.% Nb in 5 wt.% fissium [1.4]. These alloying elements also facilitate in improving the structural integrity of the fuel under irradiation and lower the fuel-clad chemical interaction. Mo is the main component of fissium and it 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 an 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'.

The composition of U-Mo alloy for reactor fuel should be chosen such that it preferably has an isotropic γ -BCC phase in the temperature range relevant to reactor operation. The BCC crystal structure ensures isotropic physical and mechanical properties like swelling and thermal conductivity etc. One of the life-limiting phenomena of metallic fuel is fuel-clad chemical interaction. Till now, this reduction in FCCI is partially achieved through alloying U with zirconium which forms a ZrN barrier layer during fabrication stage and Zr layer during operation. However, some reports indicate that this layer/rind may generate cracks or defects during operation and cause a higher rate of interaction near the defects. U-Zr alloys are extensively studied both in-pile and out-of-pile. However, investigations reported on U-Mo fuel are very limited. Therefore, in the present dissertation extensive studies of U-Mo system were carried out.

1.2 Motivation

U-Zr and U-Mo based systems are identified by scientific community as possible metallic fuel materials for fast reactors. Presently, a lot of study have been conducted in U-Zr systems. However, studies of U-Mo systems for fast reactor applications are still in the nascent stage. Therefore, the present work is focused on microstructure and clad-compatibility behaviour of U-Mo binary fuel system.

With increasing Mo content, the melting point, gamma stability and swelling resistance of U-Mo alloy fuel, are found to increase. This increase in melting point makes the fuel safer during reactor operation. Microstructural analysis of U-Mo fuel containing more than 9-10 wt.% (\approx 22 at.% Mo) is not available in literature. Interaction of U-Mo fuel with Fe based clad is also not available in the required temperature range.

As the metallic fuel is made through melting and casting route, detailed characterization of as-cast microstructures using optical microscope, Scanning Electron Microscope, X-ray diffraction analysis and micro hardness measurement is utmost important. Electron back scattered diffraction analysis is also required to know the presence of texture as textured material is supposed to give dimensional instability during reactor operation.

For the last three decades, dendritic solidification through phase field technique has been proven to be one of the advanced techniques to study dendritic crystal growth in mesoscale. The growth of dendritic crystal is an interface dominated phenomena. Thermal supercooling and compositional super saturation in solid-liquid interface have pronounced effect on the crystal growth process. The solid-liquid interface at low undercooling is considered to be in local equilibrium. In phase field modeling, interface is considered as diffuse in nature, therefore explicit tracking of interface is not required. However, for quantitative phase field modeling at real space and time scales, thermodynamic and mobility databases are required as model input parameters. The development of quantitative phase field model for solidification of U-Mo alloys is required to predict the microstructural evolution during solidification and associated micro-segregation of Mo in dendritic microstructures during casting of U-Mo metallic fuel. This study will enhance the mechanistic understanding of the process during fabrication of the fuel.

1.3 Objectives Of The Work

The objective of the present dissertation is to understand of U-Mo alloy for its use as fast reactor fuel. In order to achieve this, microstructural analysis of different compositions of U-Mo alloys was carried out. All these alloys were stable as BCC- γ phase at high temperature. To further understand the effect of molybdenum addition on the fuel behaviour, extensive studies were carried out on 33 at.% Mo alloy. According to the equilibrium diagram, this composition corresponds to the only intermetallic compound of this binary system. This is also the highest Mo content in uranium that does not give precipitates of molybdenum at lower temperature, in an equilibrium condition.

One of the life-limiting factors of fast breeder reactor clad is the fuel clad chemical interaction (FCCI) due to formation of low melting eutectics between U and Fe. This chemical interaction should be avoided or minimized to increase the fuel burn-up. Presently, U-Pu-Zr is considered as a standard option for metallic fuelled fast reactor fuel cycle. One of the main advantages of U-Pu-Zr metallic fuel is the formation of Zr rind outside fuel surface during fabrication which minimizes FCCI through raising the eutectic temperature. It is important to investigate whether addition of Mo in the metallic fuel can also help in improving FCCI. Mo has high melting point and good thermal conductivity and its addition help in increasing solidus temperature. It was important to establish whether its addition can also improve FCCI , an important criterion for consideration of Mo addition in metallic fuel, for fast reactor fuel programme. To achieve the set objectives, the following tasks were identified.

(a) U-Mo alloys may have various types of microstructures depending upon the composition of the alloy and heat treatment given to them. Micro-structural characterization and Rietveld Analysis of four different U-Mo alloy fuels (2, 5, 10 and 33 at.% Mo) in as-cast and annealed conditions, was one of the main objectives of the thesis. This analysis is required for better mechanistic understanding of microstructure evolution of the fuel with increasing Mo content.

(b) To establish a correlation of hardness of the alloy with Mo content in U-Mo fuel.

(c) EBSD analysis of as-cast U-33 at.% Mo alloy for studying preferred orientation and segregation pattern in the microstructure.

(d) Development of Phase Field model for U-33 at.% Mo alloy to predict the microstructure and segregation pattern during solidification is another important objective of the thesis, as most of the metallic fast reactor fuels are fabricated through melting and casting route.

(e) Investigation of chemical interaction of U-33 at.% Mo with T91 cladding material at different temperatures. This is one of the most important criteria for accepting the proposed alloy as a reactor fuel.

1.4 Organization Of Thesis

Keeping the above objectives in mind, the present thesis is organized in the following chapters:

- The literature review related to metallic fuels which are the candidate material for the fast reactor applications are discussed in the second chapter. This chapter also discusses the phase diagrams of the possible binary and ternary fuel materials. The general in-pile behaviour of metallic fuels are also discussed in this chapter.
- The experimental details of the alloy preparation methods, heat treatments and different techniques used for characterization of alloy are discussed in third chapter.
- The results of microstructural and micro-chemical characterization of different U-Mo fuels in as-cast condition, as well as, after annealing treatment are described in fourth chapter.
- In next chapter, a detailed description of phase field model (PFM) developed to
 predict the microstructure evolution during solidification of U-Mo alloys are given.
 The main objective of this work was to understand the important parameters that
 affect the microstructural evolution of U-33at.% Mo during solidification and
 associated micro-segregation of Mo in dendritic microstructures during casting of U-Mo metallic fuel.
- In sixth chapter, a detailed study of fuel clad chemical interaction between U-33at.%
 Mo with T91 (9Cr-1Mo-Bal.Fe) alloys are described.
- Major findings and future roadmap are given in seventh chapter.

1.5 References

1.1 S. C. Chetal , P. Chellapandi, Indian fast reactor technology: Current status and future programme, Sadhana 38(5) (2013) 795–815.

1.2 Containment Source Terms for Sodium-Cooled Fast Reactor Accidents, Thesis by Marissa Umbel, Ohio State University,2011.

D.E. Burkes, R.S. Fielding, D.L. Porter, D.C. Crawford, M.K. Meyer, J. Nucl. Mater.
 389(3)(2009), 458–469.

1.4 Technical rationale for metal fuel in fast reactors, Y. I. Chang, Nuc. Engg. Tech39(3)(2007),161-170.

Chapter 2: Literature Review

The economic incentive of nuclear power can be harnessed more with increase in fuel burn-up of reactors which in turn reduce fuel cycle cost and produce cheap nuclear power. India is developing metallic fuel fast breeder reactors for deployment in near future. The main advantages of metallic fuels over conventional ceramic fuels are high breeding ratio, higher thermal conductivity and better in-reactor behaviour during transient conditions. Worldwide, number of fast reactors [Table 2.1] have irradiated MOX and/or metallic fuel. A significant number of metallic fuel rods of U-Zr, U-Pu-Zr, U-Mo and U-fissium have been burnt in those reactors. This chapter gives a review of different metallic fuel and its irradiation performance.

Reactor	Country	Ther. power MW	El.output MWe	Dates of Operation
Clementine	USA	0.025	NA	1946–1952
EBR-I	US	1.0	NA	1951-1963
BR-2	USSR	0.1	NA	1956–1958
BR-5/BR-10	Russia	8	NA	1958-2002
DFR	UK	72	15	1959-1977
EBR-II	US	62.5	20	1964-1994
Fermi-1	US	200	NA	1963-1972
Rapsodie	France	40	NA	1967-1983
BOR-60	Russia	60	NA	1968-
BM-40A	USSR	155	NA	1969–1990
BN-350	Kazakhstan	1000	90	1972–1999
KNK-II	Germany	58	NA	1972-1991
Phenix	France	590	264	1973–2009
PFR	UK	600	NA	1974-1994
FFTF	US	400	NA	1980-1992
BN-600	Russia	1470	600	1980–pres
JOYO	Japan		140	1982
Superphenix	France	3000	1242	1985–1998
Monju	Japan	714	280	1980–1992
FBTR	India	42.5	NA	1985-Present

Table 2.1: History of fast reactor [2.1-2.3]

2.1 Pure Elements: Uranium, Plutonium, Molybdenum, Zirconium

Nuclear grade uranium is produced through solvent extraction process [2.4]. Majority of Uranium is found in earth as Uraninite (pitchblende) which is combination of UO₂ and U₃O₈. Uranium has three stable allotropic phases, orthorhombic α -U (-231 °C to 667.3 °C, 4 atoms/cell: a≠b≠c, a = 285.4 pm, b = 587 pm, c = 495.5 pm), tetragonal β-U (667.3 °C to 774.8 °C, 30 atoms/cell: a ≠ b=c, α =β= γ =90°, a = 565.6 pm, b = c = 1075.9 pm) [2.5] and body-centered cubic γ -U (774.8 °C to 1135 °C, 2 atoms/cell; a =b=c= 352.4 pm, α =β= γ =90°). The most common isotopes in natural uranium are ²³⁸U (99.27%) and ²³⁵U (0.72%).²³⁵U is a fissile material.

In nuclear reactor, Plutonium (Pu) is produced due to capture of neutron. The spent fuel discharged from reactors contains significant amount of Pu of various isotopes (Pu^{238} to Pu^{242}). The Pu is extracted from nuclear fuel through PUREX process. It is a solvent extraction process , in which Tri-n-butylphosphate (TBP) diluted in dodecane is used as solvent for extraction of uranium and plutonium.

Plutonium has six solid state allotropes. These are primitive monoclinic plutonium (α), body-centred monoclinic plutonium(β), face-centred orthorhombic plutonium (γ), face-centred cubic plutonium (δ), face-centred tetragonal plutonium (δ '), body-centred cubic plutonium (ϵ). The melting point of pure Pu is 640 °C.

Zirconium is produced from zirconium chloride through Kroll's process. Crystal structure of pure Zr at room temperature is hexagonal closed packed (hcp α) with c/a 1.593. HCP structure has significant anisotropy. At 865°C, pure Zr undergoes an allotropic transformation from the low temperature hcp phase to body centered cubic (bcc β) phase. The melting of pure Zr occurs at 1860°C, and thus Zr can be considered as a slightly refractory metal.

Mo is extracted from molybdenite (MoS₂) ore. The crystal structure of Mo is bcc. It is also a refractory metal with a melting point of 2623°C. Mo has higher thermal conductivity

than Zr [2.5, 2.6]. In comparison to Mo, Zr has lower neutronic absorption cross-section (Zr = 0.18 b, Mo = 2.48 b) [2.7] in thermal spectrum (0.025 eV) region. However, in fast spectrum region (1 MeV, $Zr = 2.41 \times 10^{-2}$ b and Mo = 3.48×10^{-2} b) [2.8], there is no significant difference between these two elements.

2.2 Alloying Elements Of U Based Alloys

In metallic alloy fuel uranium fuel is alloyed with transition group elements (4d and 5d elements in Group IV through VIII). These alloying elements e.g., Zr, Mo, Nb, Ti and fissium (Fs stands for fissium, which is a mixture of Mo, Ru, Rh, Pd, Zr and Nb) form solid solutions with γ -U and provide viable alternatives as the fast reactor driver fuel. The addition of Pu to U lowers the allotropic transformation temperature and melting point of U-Pu alloy. A minimum in the liquidus-solidus curves occurs at 12 at.% U and 610 °C. Pu and U binary forms two intermediate phases: η and ξ . ξ is stable at room temperature. The maximum solubilities of U in Pu allotropes are (α -Pu),<0.2 at.% U; (β -Pu), 2 at.% U; (γ -Pu), 0.7 at.% U; and (δ -Pu), 0.3 at.% U [2.9].

The prominent metallic fuel systems which are irradiated in fast reactors are:

(1) U-Zr and U-Pu-Zr

(2) U-Mo and U-Pu-Mo.

These systems and their irradiation experience are described here:

2.2.1 U-Zr and U-Pu-Zr Alloying of U with Zr increases the melting point of the fuel as shown in U-Zr phase diagram [Fig. 2.1]. Alloying of U with Zr increases the melting point of the fuel as shown in U-Zr phase diagram. The Pu-Zr diagram is given in Fig.2.2. The most important feature of this diagram is the continuous solid solubility of ε -Pu with β -Zr with increasing solidus from Pu to Zr. The diagram is characterized by the presence of two intermediate phases (Pu₆Zr (orthorhombic), PuZr₂ (hexagonal)) and extended δ -Pu solid

solubility (\approx 45 wt.% Zr). This gives rise to two eutectoid reactions and a large α -Zr solubility (20 wt.% Pu).







Fig. 2.2 Pu-Zr binary phase diagram [2.10].
Alloying of U with Zr increases the melting point of the fuel as shown in U-Zr phase diagram (Fig.2.1). The γ phase exhibits full mutual solid solubility of U with β -Zr at high temperature. Whereas, α -U and β -U allotropes of uranium have limited solid solubility of Zr (maximum solubility of Zr in β -U and α -U are 1at.% Zr at 692 °C and ~ 0.6 at.% Zr max. at 662 °C, respectively). α -Zr has very little solubility of U upto 865°C. There are two invariant reactions in Uranium side (693°, 662°C) of the U-Zr binary phase diagram and hexagonal δ (UZr₂) phase formation occurs in between 66-78 at.% Zr. The reaction kinetics for the $\gamma \rightarrow \delta$ phase formation is so sluggish that cubic bcc-phase remains at room temperature during non equilibrium cooling. Addition of 10% Zr in U/ Pu fuel, increases ternary alloy solidus temperature while maintaining liquidus low enough for injection casting in quartz. U-Zr/U-Pu-Zr fuel has good compatibility with cladding and also increases fuel cladding eutectic temperatures.

The irradiation experience of metallic U-Zr and U-Pu-Zr [2.11] pins, which are irradiated in EBR II [2.12, 2.13] and FFTF, are well documented. In FFTF a series of metallic fuel of U-10 wt.% Zr which is sodium bonded in HT9 clad were irradiated. The important irradiation phenomena of the metallic fuel are [2.14].

1) Swelling - fission gas and solid fission product

- 2) Fuel clad mechanical interaction
- 3) Fuel clad chemical interaction

Dimensional instability is one of the important concern in metallic fast reactor fuels. Dimensional instability can occur due to irradiation growth, grain boundary mechanical cavitation, fission gas (Xe/Kr) swelling and solid fission product swelling. The U-Zr is a multi-phase fuel. In the periphery of the fuel, temperature may be low enough to be stable as α phase of the fuel, which is anisotropic. Anisotropic characteristic of the fuel is responsible for dimensional instability of the fuel slug like irradiation growth. Irradiation growth happen in α -U, which has orthorhombic crystal structure, due to [010] elongation and [100] shrinkage. The elongation happen due to anisotropic condensation of interstitial and vacancy loops in the lattice. In random polycrystalline due to anisotropy there is mismatch of growth, which generate cavitation type defect at the grain boundary. This phenomena is further enhanced by presence of macroscopic texture in the fuel slug. Through alloying or heat treatment, randomization of the grains are achieved which prevents anisotropic growth of the fuels.

The irradiation of metallic fuel causes fission of radio-isotopes, resulting in generation of solid and gaseous fission product. The fission gases (Xe+Kr) which are ~25% of all fission product contribute immensely to swelling. The gaseous fission product generate bubble after coalescing and cause swelling. Under neutron irradiation, gas bubbles evolve and enhance the formation of cavities and cracks. Similarly, solid fission products (Mo, Ru, Zr, Pd and lanthanides) accumulate with burn-up and cause swelling.

The cracking of fuel causes ingress of bonded sodium in the fuel and changes effective conductivity of the fuel. Swelling of the fuel, at 1-2 at.% of burn-up, result in close contact between fuel slug and clad. As a result, sodium is squeezed out to the plenum region. This causes fuel clad mechanical (FCMI) and chemical interaction (FCCI). Fuel power at a particular radial ring depends on the actinide concentration in the ring, and change of fuel conductivity due to the evolution of porosity. The swelling causes reduction of thermal conductivity in fuel. Initially, fuel conductivity decreases to ~50% of the beginning of life (BOL) value, until 0.75 at.% burn up. Then thermal conductivity increases linearly up to 70% at 1.5 at.% burn up. This increase is due to infiltration of sodium into the pores and cracks which are generated through swelling. After 1.5 at.% burn up, the fuel conductivity does not change significantly (~70% of the BOL value) [2.15].

The migration of fuel constituents under thermal gradient turns the as-fabricated U-Zr/U-Pu-Zr metallic alloy into a radially multiphase fuel. The migration of elements occurs due to temperature gradient and also due to stability of different phases in different temperature zones. In central high temperature zone the cubic solid-solution is stable, whereas, at the peripheral region (U,Pu)Zr₂ is stable. This migration of fuel constituents changes the properties locally and affects almost all other fuel behaviours. In ternary fuel U-Pu-Zr plutonium content higher than ~7 at. % (8 wt.% Pu), causes higher level of constituent redistribution in the early stage of irradiation and lead to formation of 3 radial fuel zones [2.15, 2.16]. In the Irradiated U-Pu-Zr fuels, three distinct concentric zones were (Fig. 2.3), viz., a Zr-enriched central zone, a Zr depleted and U-enriched intermediate zone, and a slightly Zr-enriched zone on the outer periphery [2.15]. The annular zone structure is also characterized by distinct differences in porosity.

Generally, U concentration profile is opposite to that of Zr and Pu concentration profile remains virtually unchanged. The higher concentration of Zr atoms at the centre location, raises the fuel solidus temperature at the peak temperature region and at the periphery region, it enhances the fuel-cladding compatibility. However, it decreases fuel solidus temperature in the intermediate region of the fuel. Additionally, it causes high rate of fuel swelling which lead to peripheral crack formation in the fuel [2.16].



Fig. 2.3 Cross-sectional photomicrograph of the post-irradiated fuel along with EPMA scan of U, Zr and Pu [2.15].

2.2.2 U-Mo and U-Pu-Mo

To increase the burn-up potential of fast reactor further, U-Mo and U-Pu-Mo ternary metallic fuels can be developed as a fast reactor fuel. Modification in neutronics and reactivity due to addition of higher amount of Mo (2.6 barn neutron cross section) can be compensated with improved reactor and fuel design [2.17].

Mo has limited solubility in α -(U) and β -(U), whereas γ phase has significant solid solubility. The U-Mo binary phase diagram is given in Fig. 2.4 which is characterized by the following invariant reactions. Peritectic reaction at 1302°C, L+bcc(Mo) $\rightarrow\gamma$ -U, and eutectoid reaction at 569°C, $\gamma \rightarrow \alpha$ U+U₂Mo. The kinetics of the ordered U₂Mo phase formation is very sluggish.



Fig. 2.5 Pu-Mo binary phase diagram [2.10].

Increasing of Mo content in U-Mo fuel results in increase of melting point as well as γ -phase stability. Lowest temperature of γ -phase stability, eutectoid temperature, is observed at

21.6 at.% (10 wt.%) Mo. An alloy with 33 at.% Mo also shows wide temperature range of γ phase stability and an increase in solidus temperature by ~ 60 °C. The advantage of U-Mo over U-Zr is that, Mo is better γ stabilizer than Zr, because it can stabilize γ -phase to much lower temperatures ($T_{eutectoid}^{U-Mo} = 555^{\circ} C$ and $T_{eutectoid}^{U-Zr} = 690^{\circ} C$). The U-Mo fuel shows higher melting point (solidus temperature) with increasing Mo content, in the range of 8-40 at.% Mo, however, U-Zr shows increase of solidus temperature from the beginning i.e. 0-100 % of Zr. According to equilibrium phase diagram, the alloy with ~ 33 at.% Mo forms a tetragonal U₂Mo phase below ~600 °C, however, during reactor operation the cubic γ -(U) phase will remain in metastable state even below 600 °C. This is due to irradiation induced phase reversion γ -phase [2.18, 2.19] and sluggish transformation kinetics of γ to α -U(orthorhombic)+ U₂Mo(tetragonal) transformation . This results in retention of γ -phase even near slug surface temperatures. As the cubic phase is isotropic, it provides advantage of isotropic expansion and uniform thermo-physical property, like thermal conductivity. The cubic (open structure) BCC phase also has advantage of higher solubility of alloying elements, which minimizes fuel constituent migration [2. 20].

Higher melting point of the fuel ensures higher safety margin for fuel melting during off-normal condition. Therefore, higher melting point greater safety margin for reactor operation. U-33 at% Mo has the highest melting point (~1236 °C) among (U-22. at.% Mo (~1183 °C)) U-rich alloys in U-Mo system. Even a rise of ~50 °C in melting point (solidus point) is significant for metallic fuels as these alloy compositions have reasonably high thermal conductivity ~30 W/mK. The high thermal conductivity ensures less heat retention in the central slug zone, thus preventing rapid temperature rise of fuel during off normal reactor operation. The higher melting point also restricts severity of fuel clad chemical interaction [2.16].

The BCC phase of Mo-Pu has high positive heat of formation, which results into phase separation of Pu and Mo [Fig. 2.5]. In Mo-Pu binary system an eutectic invariant line located at 625°C. No intermediate phases are found in the binary phase diagram. U-Pu-Mo metallic fuel has higher thermal conductivity and lower thermal expansion than U-Pu-Zr [2.21]. U-Pu-Mo also shows lower constituent redistribution in reactors than U-Pu-Zr [2.23].



Fig. 2.6 U–19Pu–10Zr pseudo-binary phase diagram . The vertical broken line indicates the phase field of U–19Pu–10Mo in typical reactor operations [2.24].

The comparison of U-17Pu-23Zr (U-19Pu-10Zr in wt.%) (Fig.2.5) with U-16.5Pu-21.5Mo (U-19Pu 10Mo in wt.%) (Fig.2.6) shows U-Pu-Zr has mixture of phases whereas U-Pu-Mo composed of single phase in reactor operating temperature i.e. 550-750 °C.



Fig. 2.7. Isopleth of U/Pu = 3. The vertical broken line indicates the phase of U-19Pu-10Mo in typical reactor operations [2.24].

As different phase may have different solubility of the constituent elements as well as fission products, so these may present appreciable driving force for migration (chemical potential gradient as well as thermal gradient) in case of U-Pu-Zr fuel. Whereas in single phase fuel, constituent migration can occur only due to thermal gradient which is significantly less in metallic fuel compared to ceramic fuel. Moreover, U-17Pu-23Zr shows α phase at lower temperature which is detrimental to swelling property of the fuel. However, U-Pu-Mo shows γ phase even at lower temperature.

2.3 Fuel clad mechanical and chemical interaction (FCCI) in metallic fuel

During in pile irradiation fission gases, like Xe, Kr, are generated which result in fuel slug swelling and the swollen fuel slug comes in contact with the cladding. Simultaneously, the progression of coalescence among the pores causes formation of open pores that are connected to the outside of the slug. Through these open pores, fission gases come outside and the bond-sodium goes into the slug. The released fission gases accumulate in the gas plenum and can increase internal pressure of the pin. The swollen fuel slug is restrained and compressed by the cladding, while it pushes out the cladding. In earlier metallic fuel designs, the smear density was kept at 85%. This caused fuel failure due to this action-reaction which is called fuel clad mechanical interaction (FCMI). In the advanced design, the fuel smeared density is brought down below 75% [2.16]. The ingression of bond-sodium recovers the effective thermal conductivity of the slug. The compressive stress applied to the swollen slug causes decrease in the open pore volume, which relaxes FCMI. The reduction of smear density to < 75% has shown favourable results in terms of FCMI, however, FCCI is still a major cause of concern. Due to contact of fuel slug with the clad, the chemical interaction reduces the effective thickness of the cladding and increases the local cladding stress. FCCI is characterized by the inter-diffusion of fuel constituents, rare earths and lanthanides and cladding constituents, like Fe. The equilibrium phases of U-Zr-Fe system can be determined from its ternary phase diagram, therefore, a phase diagram of this system is given at near cladding temperature of 650 °C (Fig. 2.29). The results of diffusion couple experiments are show in Fig. 2.8 to compare the kinetic observations with equilibrium phase-diagram.

The U-Zr-Fe diffusion couple reaction shows the formation of a number of phase layers (Fig.2.9) [2.24]. These phase layers are single phase or a mixture of phases. Concentration profile analysis of each element in these phase layers can generate diffusion path of the layer structure. This diffusion path corresponds to the sequence of compositions developed in the layer structure. The diffusion path is shown in ternary isothermal diagram in Fig. 2.8. The diffusion path imposed on ternary diagram shows that Fe penetrated inside the fuel and generated equilibrium phases; like. UFe₂, U₆Fe, ZrFe₂ etc. Similarly, U penetrated in the cladding to generate UFe₂ in clad which decreased effective thickness of the Fe clad.



Fig.2.8: U-Zr-Fe ternary phase diagram [2.24] and diffusion path(dotted gray lines) at 650 °C. Open circles indicate approximate average compositions of the layers.



Fig. 2.9: Backscattered electron micrographs from U-10 wt%Zr vs Fe diffusion couple

annealed at 650 °C for 400 h [2.24].

2.4 Reference

2.1 J. I. Sackett, EBR-II Test and Operating Experience,

www.arcnuclear.com/uploads/File/EBR-II-oper-exp%20-12-5-08-sackett.pdf.

2.2 P. Mazgaj, P. Darnowski, S. Gurgacz, M. Lipka, K. Dziubanii, J. Power Tech. 94 (Nuclear Issue) (2014) 16–26.

2.3 IAEA Technical Reports, Design Features and Operating Experience of ExperimentalFast Nuclear Energy, NP-T-1.9, Vienna, 2013.

2.3 Uranium Extraction Technology, Technical Report series no. 359, IAEA publication, https://www-pub.iaea.org/MTCD/Publications/PDF/trs359_web.pdf.

2.4 First-Principles Study of Properties of Alpha Uranium Crystal and Seven Alpha Uranium Surfaces, J. Chem. 8618340 (2017), https://doi.org/10.1155/2017/8618340.

2.5 J.K. Fink, L. Leibowitz, J. Nucl. Mater 226 (1995) 44-50.

2.6 https://www.plansee.com/en/materials/molybdenum.html.

2.7 A.N Shmelev and B K Kozhahmet, J. Phys. Conf. Series 781 (2017) 012022. doi:10.1088/1742-6596/781/1/012022.

2.8 Atlas of Neutron Capture Cross Sections, Nuclear Data Section, International Atomic Energy Agency, https://nucleus.iaea.org/Pages/ngatlas.aspx.

2.9 Thermodynamics and phase diagrams of the plutonium-uranium, uranium-zirconium, plutonium-zirconium and plutonium-uranium-zirconium systems, R Agarwal, V Venugopal, http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/36/097/36097360.pdf.

2.10 ASM International, ASM Handbook Volume 3: Alloy Phase Diagrams, 1992.

2.11 W. J. Carmack, H.M. Chichester, D. L. Porter, D. W. Wootan, J. Nucl. Mater. 473 (2016) 167-177.

2.12 D. E. Burkes, R. S. Fielding, D. L. Porter, D. C. Crawford, M. K. Meyer, J. Nucl. Mater. 389(3)(2009), 458-469.

2.13 R.G. Pahl, D.L. Porter, C.E. Lahm, G.L. Hofman, Metal. Trans. A 21A (1990) 1863-1870.

2.14 T Ogata, Y.S. Kim, A.M. Yacout, 3.23-Metal fuel performance modeling and simulation, Comp. Nuc. Mater. 3(2012) 713-753.

2.15 Y. S. Kim, S.L. Hayes, G.L. Hofman, A.M. Yacout, J. Nucl. Mater.359 (2006) 1728.

2.16 Y. I. Chang, Nuc. engg .tech 39(3)(2007),161-170.

2.17 R. D. Mariani, D. L. Porter, S. L. Hayes, J. R. Kennedy: Metallic Fuels: The EBR-II Legacy and Recent Advances, Proc. Chem.7 (2012) 513 - 520.

2.18 M.K. Meyer, J. Gan, J.F Jue, D.D. Keisar, E. Perez, A. Robinson, D.M. Wachs, N. Woolstenhulme, G.L. Hofman, Y.S. Kim: Irradiation performance of U-Mo monolithic fuel, Nuc. Engg. Tech., 46(2) (2014) 169-182.

2.19 M.L. Bleiberg, L.J. Jones, B. Lustman, J. App. Phys., 27(11)(1956) 1270-1283.

2.20 R.D. Mariani, D.L. Porter, V.S. Blackwood, Z.S. Jones, D.L. Olson, B.Mishra, J.R. Kennedy, S.L. Hayes: International Conference on Fast Reactors and Related Fuel Cyles: Safe technologies and Sustainable Scenarios (FR13), Paris, France,4-7 March,2013 IAEA-CN--199/366; ISSN 0074-1884.

2.21 A. Landa, P. Soderlind, B. Grabowski, P. E. A. Turchi, A. V. Ruban, L. Vitos: Ab initio study of advanced metallic nuclear fuels for fast breeder reactors, MRS Spring Meeting, San Francisco, CA, USA, April 9-13, 2012, published in the MRS Proceedings on "Actinides - Basic Science, Applications, and Technology", 14 pages (LLNL-CONF-552336).

2.22 P.E.A. Turchi, A.I. Landa, Thermodynamic database, lower length scale PartI: Thermodynamic assessment of the ternary alloy system Mo-Pu-U(M3MS-12LL0602091), LLNL-TR-553775(2012).

2.23 Y. S. Kim, G.L. Hofman, A.M. Yacout, T.K. Kim, J. Nuc. Mater., 441(1-3), (2013), 520-524.

2.24 K. Nakamura, T. Ogata, M. Kurata, A. Itoh, M. Akabori, Journal of Nuclear Materials 275 (1999) 246-254.

Chapter 3: Materials and Methodology

This chapter describes details of materials used for preparation of alloys, subsequent heat treatments and characterization techniques used during this study. It also gives details of fuel-clad compatibility testing capsules.

3.1 Material

Four different compositions of U-Mo alloys (2, 5, 10 and 33 at.% Mo) were initially prepared by arc-melting with required amounts of starting metallic uranium slug (99.86 wt.%) and 99.9 % pure Mo. The starting materials were thoroughly degreased with 5% phosphoric acid solution, before melting. Alloys were arc-melted repeatedly in high purity argon atmosphere (99.999% purity) and after each melting, the alloy button was turned upside down for complete homogenization of Mo in U and these steps were repeated 4-5 times to ensure homogeneity of the alloy. These alloys which were cooled by water-cooled copper hearth at the bottom were treated as as-cast alloys. Adequate precautions like repeated purging of the arc melting chamber, purity of argon gas etc. were taken to minimize impurity pick-up during melting operation. The alloys were cut into pieces having thickness 3-5 mm and prepared metallographically.

T91, is a ferritic steel (9Cr-1Mo-0.35Si-0.45Mn-0.22V) (in wt.%) and shows better irradiation behaviour than austenitic steel. Hence, this alloy is considered as advanced clad material for fast reactor fuel. T91 alloy having 1 mm thickness was cut and polished metallographically.

3.2 Arc melting Furnace:

Arc melting furnace (Fig.3.1) consists of a standard Tungsten Inert Gas (TIG) welding unit, chiller and vacuum unit. In arc melting furnace tungsten Inert Gas (TIG) welding unit acts as a power source and chiller unit is used to cool the copper hearth. Copper hearth is the container of the alloy metals and also acts as one of the electrodes. Continuous cooling of the hearth with chilled water ensures that copper impurities don't contaminate the samples during arc-melting. The mobile electrode is made up of tungsten. The chamber is evacuated with rotary and diffusion pump before flushing it with high purity Ar-gas (99.999 % purity). Arc generated by power source, is struck between the tungsten electrode and the metals in the crucible, is used to melt the metals to form an alloy. The arc melting chamber is evacuated and then back filled repeatedly with argon gas to prevent air contamination. The metal can be heated to a temperature more than 3000 °C.



Fig. 3.1 The vacuum Arc melting unit along with schematic of arc melting system [3.1].

3.3 Thermal Treatment

To prepare equilibrium structure alloys of different compositions from as-cast alloys, these alloys were annealed in quartz capsules. Annealing of these U-Mo alloys was carried out by wrapping the alloy buttons in a tantalum foil and encapsulating them in quartz tubes with helium cover gas, filled at 100 mmHg. 'He' was filled after evacuation for 1-2 mins. The annealing was done for long duration, at different temperatures, to achieve equilibrium microstructure at ambient temperature. Initially, all the alloys were held at 900°C, for 140

hrs. then slow-cooled (~0.1 °C/s) to 500°C. The quartz capsules were held at 500°C for another 140 hrs., after which slow cooled to ambient temperature (Table 3.1). These samples were referred as annealed samples.

Temperature	U- 2 at. %Mo	U- 5 at. %Mo	U- 10 at. %Mo	U- 33 at. %Mo	
°C	(h)	(h)	(h)	(h)	
900	140	140	140	140	
500	140	140	140	140	

Table 3.1 Heat treatment of U-Mo alloys



Fig. 3.2 U-Mo TTT Diagram [3.2].

3.4 Fabrication Of Diffusion Couples And Thermal Treatment

For diffusion couple experiments, all the mating surfaces of annealed U-33at.% Mo/T91 diffusion couple were polished using silicon carbide papers (240, 600, 800 and 1200

grit), using ethanol as a lubricant to minimize oxidation. Then a ~3 mm thick polished disk of U-33 at.% Mo were sandwiched in two 1 mm thick T91 alloy disks. The T91 material was received from Quality Assurance Division, Bhabha Atomic research Centre. This ferritic martensitic steel was used in the standard normalized and tempered condition. The heat treatment of as-received T91 consisted of normalising heat-treatment at 1050 °C for 1 min per mm thickness and tempered at 770 °C for 3 minutes per mm followed by air cooling. These disks were encapsulated in Tantalum foils and clamped in inconel jig. Encapsulation with Tantalum foils was done to prevent interaction between the diffusion couples with Inconel 600 jig. The lid of the fixture had an screw which applied uniform pressure on diffusion couple. To minimize oxidation of the material during heating assembled diffusion couples were sealed in quartz tubes (Fig.3.3-3.4), filled with helium cover gas, at 100 mmHg pressure.



Fig. 3.3 Glass sealing of diffusion couple.



Fig. 3.4 Engineering drawing of the diffusion couple.



Fig. 3.5 Cross sectional view of the diffusion couple indicates presence of Ta foil surrounding the T91 to prevent interaction between diffusion couple and jig.

These sealed coupons were heated in a tubular furnace at 650°C for 14, 30, 85 days, 675 °C for 7, 14, 40 days and 700°C for 3, 7, 15 days. After heat treatment, diffusion couples were mounted in epoxy and cross-sectioned. The epoxy mounting of the sample prevented oxidation during metallography and also kept the components intact during sample preparation. Diffusion couples were prepared up to 1 μ m surface finish for observation under SEM. Low magnification SEM image (Fig. 3.5) of the diffusion couple indicates the presence of Ta foil surrounding the T91.

3.5 Optical Microscopy

For optical microscopy (Model No: Axio Observer.A1m Make: Carl Zeiss , Germany), as-cast and annealed samples were polished mechanically (up to 600-grit SiC paper and diamond cloth) and then electro-etched in 5% H₃PO₄ aqueous solution with SS304 cathode, at a constant 2V DC.

3.6 Scanning Electron Microscopy with EDS analysis

Scanning electron microscope (SEM) is a type of electron microscope with high depth of field. Hence, three dimensional fracture surface imaging is possible with SEM. The high energy electron beam generated from SEM electron gun is focused with magnetic condensing lens and a scanning coil. Resolution achieved in standard FEG -SEM can be 1-5 nm.

Schematic diagram of scanning electron microscope is given in Fig. 3.5. When the accelerated primary electrons strikes the sample, it produces very low energy secondary electrons (SE) from the surface (5-50 nm), high energy back scattered electrons (BSE) (450 nm), and characteristic X-rays (2-5 µm).



Fig. 3.6 Schematic diagram of scanning electron microscope [3.3]

BSE imaging gives atomic number contrast and Energy dispersive spectroscopy (EDS) using the characteristic X-ray identifies the chemical composition in a region of $\sim 1 \,\mu m$ diameter and $\sim 1 \,\mu m$ depth of specimen. Scintillation crystal based detector is used for detecting BSEs. Whereas, Everhart-Thornley (E-T) detector, a type of scintillator-photomultiplier, is used for collecting SE signal.

EDS systems consists of a sensitive x-ray detector, and software to collect and analyze energy spectra. Presently "silicon drift detectors" that operate at higher count rates without liquid nitrogen cooling is used for EDS analysis. The crystallographic analysis is possible SEM when EBSD system is attached with it,. Hence, microstructural characterization, chemical composition and crystallography are possible in SEM with EDS and EBSD. When accelerated electron strikes the sample, a typical pear shaped interaction volume (Fig. 3.7) is generated in the sample. Monte Carlo simulation gives the shapes of the interaction volume at different accelerating voltage in different material.



Fig. 3.7 Typical pear shaped interaction volume evolves when accelerated electron strikes the sample in SEM [3.4].

Specimens for scanning electron microscopy (Camscan CS3200L) were prepared by mechanical grinding and electro-etching. For U-33 at.% Mo/T91 diffusion couple, the surface of each cross-sectioned couple was polished up to 1µm surface finish, using diamond paste for microstructural and compositional analysis. The elemental analysis of different phases was carried out using an energy dispersive spectroscope (EDS) (Make: Oxford Instruments) attached to scanning electron microscope (SEM).

3.7 Electron Backscattered Diffraction (EBSD)

Crystallographic information can be obtained from EBSD attached in scanning electron microscope. When electron beam scans through the poly crystalline sample, they are in-elastically scattered, to form a divergent source of electrons close to the surface of the sample. Some of these back scattered electrons are incident on atomic planes at an angle satisfying the Bragg equation, $2d \sin\theta = n\lambda$,

where n is an integer, λ is the wavelength of the electrons (Accelerating voltage), d is the spacing of the diffracting plane, and θ the angle of incidence of the electrons on the diffracting plane.

Hence, the diffracted electrons form a set of paired large angle cones, corresponding to each diffracting plane. Kikuchi bands form on the phosphor screen when the region of cone of enhanced electron intensity intersect the screen. The pattern is a gnomonic projection of the diffracted cone, making the band edges appear hyperbolic.

The width of Kikuchi band is given $as(w) \approx n \times l \times \lambda/d$, where l is the distance from the sample to the screen. Planes with wide d-spacing generate thinner Kikuchi bands than those with narrower planes. Hence the positions of the Kikuchi bands are used to calculate the orientation of the diffracting crystal. As the symmetry and appearance of the pattern is related to a particular crystal structure and alloy composition at the incidence point of electron, the diffraction pattern is used to measure crystal orientations and to identify materials.

In a crystal orientation map, similar crystal orientations are depicted in similar colors with some angle tolerance. Each grain is represented by single colour. The orientation map are processed to identify the position of all the grains, sub-grains and grain boundaries (low angle, high angle, twin boundaries). Hence the technique is unique, as it provides link between microstructure and crystal structure. The Fig. 3.7 below shows the phosphor screen generating typical pattern from a tilted sample. This technique is extensively used in texture analysis, along with detailed microstructure characterization.



Fig. 3.8 EBSD configuration inside the SEM chamber [3.5].

For EBSD works, after getting 1 μ m surface finish in mechanical polishing, electro polishing was carried out using an agitated solution of 45% ethanol, 27% ethylene glycol, and 27% H₃PO₄ at 15 V DC, for approximately 7 sec. The EBSD scans were carried out in LaB6 CS3200L SEM fitted with a Nordlys MAX detector (HKL Technology A/S, Denmark) at 20 KV with a step size of 1 μ m. The HKL Channel 5 software (HKL Technology A/S) was used for data analysis.

3.8 Micro-hardness Measurement

Vickers hardness (Model No. FM-700, Future Tech Corporation, Tokyo, Japan) measurements were carried out using 300 gm load with 10 s dwelling time with an Vickers hardness instrument. Nine measurements on each samples were done to get the average hardness of the alloys.

3.9 X-Ray powder diffraction and Rietveld analysis

The samples were prepared metallographically. After getting 1µm surface finish, electro-polishing was carried out. As the depth of penetration of X ray is very less in U alloys, and presence of deformed layer on the surface affect the X ray profile, proper care was taken to remove the effect of cold work on the surface. After repetitive electro-polishing, X ray scan was taken to note the intensity and position of three characteristic peaks till there is no change in intensity of the peaks. The normal XRD scans were recorded on each samples in the 2 θ angle range 30°-140°, on Rigaku Ultima IV Diffractometer using CuK_a radiation in scan steps of 0.05° 2 θ / step and 0.4 ° 2 θ /min.

Rietveld refinement technique is a standard tool to analyze powder diffraction data for crystal structure analysis. Rietveld refinement can be carried out on X-ray or neutron diffraction data acquired by fixed wavelength (angle dispersive) or fixed angle (energy dispersive) method. In the present work, fixed wavelength X-ray diffraction data of U-Mo fuels were used. The samples were studied by analyzing X-Ray powder diffraction pattern (XRD) to identify, characterize and quantify the crystalline phases. The XRD pattern was acquired by Bragg-Brentano reflection geometry (θ/θ) type diffractometer, using CuKa radiation. The X-ray diffraction patterns were fitted with different adjustable parameters of background reflection, profile shape function (PSF) and crystal structure parameters with a least square algorithm. The main objective of PSF was to appropriately model angle dependent shape features of the X-ray peaks over the whole range of diffraction angles in which the data were collected. The PSF function proposed by Caglioti, Pauletti & Ricci, given by Young and Wiles [3.6] (FWHM² = U*tan θ^2 + V*tan θ^2 +W²) describes profile shape more accurately. Where, FWHM is full width at half maxima of the highest intensity peak and U, V and W are the refinable instrumental parameters. The reflection from pure annealed uranium was used for correcting instrumental broadening. The space group data of each

phase has been tabulated in Table 3.2. The XRD pattern was refined using 'MAUD' program [3.7].

Phase	Space group(Space Group no)	Atom	Wyckoff notation	Atomic Positions		Lattice parameter(nm)			
				x	У	Z	а	b	С
α-U	Cmcm(63)	U	4c	0	0.1034	0.25	0.285	0.587	0.495
α"- U	P2 ₁ /m Axis b	U	2e	0.855	0.25	0.069	0.3278	0.4977	0.3185
γ - U	Im 3 m(229)	U	2a	0	0	0	0.353	0.353	0.353
γ'- U2Mo	I4/mmm(139)	U	4e	0	0	0.328	0.343	0.343	0.983
		Mo	2a	0	0	0			
UO_2	Fm 3 m(225)	U	4a	0	0	0	0.547	0.547	0.547
		0	8c	0.25	0.25	0.25			

Table 3.2 Space group, Wyckoff notation, atomic position and lattice parameter of different phases used during Rietveld analysis [3.8].

3.10 References

3.1 http://home.iitk.ac.in/~anandh/lab/Arc_Melting.pdf.

3.2 T.A. Pedrosa, A.M. Matildes dos Santos, F.S. Lameiras, P.R. Cetlin, W.B. Ferraz,

- J. Nucl. Mater 457 (2015) 100 -117.
- 3.3 https://en.wikipedia.org/wiki/Scanning_electron_microscope.

3.4 https://www.slideshare.net/farshina/presentation-on-sem-scanning-electronmicroscope.

- 3.5 http://www.ebsd.com.
- 3.6 R.A. Young, D.B. Wiles, J. Appl. Cryst. 15 (1982) 430-438.

3.7 L. Miyagi, N. Nishiyama, Y. Wang, A. Kubo, D. V. West, R.J. Cava, T.S. Duffy, H.R. Wenk, Earth Planet. Sci. Lett. 268 (2008), 515-525.

3.8 Pearson's handbook of crystallographic data for intermetallic phases, vol. 2, editors: PVillars and L.D. Calvert, American society for Metals, 1985.

Chapter 4: Micro-structural Study and Rietveld Analysis

In the present study, different U-rich U-Mo alloys were characterized to understand the microstructural evolution of U-Mo alloys with increasing Mo concentration. The objective of this work was to compare microstructure, phase-fields and hardness of as-cast and annealed U-Mo alloys and to understand composition dependence of this behaviour. Scanning electron microscope with energy dispersive spectrometer and optical microscope have been used to characterize the morphology of as-cast and annealed alloys. The phases were also characterized with X-ray diffraction. The X-ray diffraction pattern were further analysed with Rietveld analysis. Simultaneous EDS- EBSD analysis of U-33 at.% Mo as-cast alloys was carried out to reveal the extent of segregation and dendritic pattern (through EDS) in randomly oriented poly-crystalline (through EBSD) alloy. This study was carried out for in-depth understanding of microstructural and phase evolution of U-Mo alloys as fast reactor fuel.

As seen from Table 4.1, many researchers [4.1-4.21] have carried out metallographic investigations of U-Mo system. Tangri and Williams [4.7] investigated U-Mo alloys, with 0.67 to 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 , $\beta+\alpha$ and $\beta+\alpha'$, 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.

Table 4.1. 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^1 and XRD	Yes	[4.1]
5-10	Hg quench from 900 °C	LM , XRD	NA	[4.2]
1.96- 36.78	Annealed at different temperatures and water quenched	LM,XRD, Chemical analysis	NA	[4.3]
0-30	Annealed at 950 C and 1000 °C and 'Hg', or oil quenched	LM,XRD	NA	[4.4,4.5]
2.5-15	Hg quenched from 1000 C	Hg quenched from 1000 C LM and XRD		[4.6]
0.67-11.39	Annealing at 950 °C with water& Ar quenching and air cooling	LM , XRD	NA	[4.7]
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	[4.8]
6-12.5	Annealing at 950 C and water quenched	Dilatometry, LM and XRD	NA	[4.9,4.10]
3.88	Annealed at 940 C and isothermal between 500 and 640 C	LM, SEM and XRD	NA	[4.11]
7.12-25.28	Annealed above 800 C and quenched to transformation temperature	LM ,XRD	Yes	[4.12]
5.9-10	Annealed at 940 C and water quenched	XRD	NA	[4.13]
0	As-cast; 625 C for 8h & vacuum cooling	LM , XRD	Yes	[4.14]
3.64	As-cast, Annealed; As-rolled at 625 C and 800 C; Rolled at 600 C & 800 C and γ-quenched from 800 -850 C		Yes	
9.36-21.60	As-cast alloy annealed in 900 C and air-cooled and irradiation	LM and XRD	NA	[4.15,4.16]
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	[4.17]
15.73-25.28	Hot rolling at 650 C	LM, XRD	NA	[4.18]

0-15	Splat cooling	SEM, EBSD ² and	NA	[4.19]
		XRD		
11-17	Splat cooling	XRD	NA	[4.20]
11.55, 15.73, 21.61	As-cast Annealed 300 C for 72 hrs. & 240 hrs. Annealed at 500 C for 72 &240 hrs.	LM, FE-SEM ³ , AFM ⁴ , EFM ⁵ and XRD	Yes	[4.21]

1.LM: Light microscope

2.EBSD : Electron backscatter diffraction

3.FE-SEM: Field emission scanning electron microscope

4.AFM: Atomic force microscope

5.EFM: Electrostatic force microscope

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 to ~ 11.18 at.% 'Mo' forms α "-U (monoclinic) on water-quenching. Stewart and Williams [4.13] have reported 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 [4.7] and 5.9 at.% Mo [4.13] 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 taking place in the composition region between 5-7 at.% Mo. Lehmann [4.4] and Lehman and Hills [4.5] 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 [4.10] investigated phase transitions in U-Mo alloys with 6.0 to 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 [4.13] 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. [4.11] 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 it in Pb-Sn quenching bath. Pedrosa et al. [4.21]. has reported microstructural investigation of U-23 at% Mo alloy, prepared by induction-melting the alloy in zirconia crucible (resulting in a cooling rate of ~ 0.5 °C/s.) and annealed the sample at 300°C and 500°C. In the present work, alloys were prepared by arc-melting in water-cooled Cu hearth, leading to cooling rate of ~100 °C/s. Subsequently, heat treatment of alloys involved annealing at 900 °C, mainly to re-dissolve microsegregated 'Mo'. Then the samples were furnace-cooled to 500 °C (below eutectoid temperature at 556 °C) and held there for long time, finally furnace-cooled to ambient temperature.

Most of the 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) [4.16] and are fabricated by hot-rolling and hot iso-static pressing of as-cast alloys at different temperatures. In the present study the main aim is to study U-Mo alloy for metallic rod-type fuel, meant for fast breeder reactors. These fuels are normally prepared by injection casting.

The operating temperature of metallic fuels in the reactor is 450 - 800 °C, thus U-Mo fuels having orthorhombic α -U in the microstructure can cause 'cavitation

swelling' [4.22] and high proportion of fission gas release [4.23]. The presence of isotropic γ -(U,Mo) phase improves in-pile behaviour of the alloy, e.g., swelling behaviour and dimensional stability. U-Mo alloy forms a stable uranium rich intermetallic compound U₂Mo, at T < 600 °C (Fig. 4.1). Therefore, according to phase diagram, below 600 °C, single phase γ -(U,Mo) dissociates into α -U and U₂Mo (Fig.4.1) and these two phases show different structural and thermal properties compared to γ -(U,Mo). During reactor operation, the U-Mo alloy gets annealed due to longer residence time at high temperature. The fuel pin faces a temperature gradient due to dynamics of heat production and removal. Therefore, depending upon the temperature profile, fuel may attain different microstructures across the radial cross-section.



Fig. 4.1 U-Mo phase Diagram [4.24].

4.1 Microstructure And Phase Analysis Of As-Cast Alloys

U-Mo alloy system can have different metastable phases depending upon thermomechanical treatment given during fabrication. The high temperature stable phases are: tetragonal-beta (β) and bcc-gamma (γ). The system also has a stable ordered tetragonal U₂Mo (γ') intermetallic compound with limited non-stoichiometry [4.3, 4.25]. However, this phase is optimized as a line compound by Berche et al. [4.26] and Zhang et al. [4.27]. The γ phase has two metastable phases γ_d and γ° [4.4, 4.21]. Room temperature equilibrium phase for uranium rich U-Mo alloys is orthorhombic alpha (α). However, it can exist as metastable distorted orthorhombic alpha (α ') or monoclinic alpha (α ''). The distorted orthorhombic alpha has acicular (α_a) and banded (α_b) morphology. The distorted orthorhombic alpha (α) is formed when high temperature γ -(U,Mo) is quenched. With addition of 'Mo', 'U' atom is replaced by smaller 'Mo' atom and 'b' parameter of orthorhombic lattice shrink, although 'a' and 'c' lattice parameters remain almost constant, resulting in progressive shift in 20 values of respective (021) plane. The decrease in 'b' parameter also depends upon cooling rate during quenching. With the addition of significant amount of 'Mo', formation of metastable monoclinic-uranium (α ") has been observed. The structure of monoclinic alpha (α ") can be described by angular distortion between 'a' and 'b' axis of orthorhombic α -U after significant substitution of 'U' by 'Mo' in the lattice, resulting in splitting of refractions from (111), (112) and (131) planes of XRD pattern. Significant difference between the atomic sizes of U (0.142 nm) and Mo (0.130 nm) results in increased stiffening of the alloy with increase in 'Mo' content, thus alloys with high 'Mo' content provide more resistance to shear. The high cooling rate generates high hydrostatic pressure and favor shear process, leading to the formation of distorted orthorhombic, α' -(U,Mo). However, a combination of lower cooling rate and high 'Mo' content result in reduced shearing, leading to formation of monoclinic structure. This monoclinic structure can be defined either by artificial space group $C2_1/m$ or by natural space group $P2_1/m$ [4.17]. In case of monoclinic structure, using $C2_1/m$ symmetry, the γ -angle is around 92.1°, whereas, using P2₁/m symmetry, β -angle is around 126.9°. Main differences between orthorhombic and monoclinic lattice is that β -angle (γ -angle for C2₁/m),

which is greater than 90°, whereas, all the angles in orthorhombic lattice are equal to 90°. The splitting of (111), (112) or (131) reflections is an indication of increase in the β -angle (γ -angle for C2₁/m) between 'a' and 'b' axes. This γ -angle of the monoclinic structure increases (> 90°) with decrease in cooling rate and increase in 'Mo' concentration. This will be understood from the structural analysis of as-cast alloys of U-Mo with different Mo contents discussed in the following sections.

4.1.1 U-2 at.% Mo & U-5 at.% Mo alloy:

The present investigation of as-cast U - 2 at.% and U - 5 at.% Mo, by XRD analysis showed presence of only α -U phase. It did not show splitting of diffraction lines, indicating absence of monoclinic (α'') structure. It also did not show shrinkage of 'b' lattice parameter, as (021) lines and other line peaks were not shifted to higher ' θ ' values in XRD pattern. This further confirmed that structure was indeed orthorhombic alpha, the stable phase of uranium.



Fig. 4.2. Rietveld plot for U-2 at.% Mo in as-cast condition. Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.

From experiment it is evident that these low 'Mo' alloys were needed higher cooling rate to generate metastable orthorhombic phases which was not achieved during arc-melting process (~100°C/sec). This also indicates that cooling by water circulated hearth in arc-melting is not equivalent to water quenching of the samples. Water quenched samples of Tangri & Williams [4.7] gave α ' structure for these compositions. The Rietveld analysis of the present XRD data for as-cast U-2 at.% Mo (Fig. 4.2) and as-cast U-5 at.% Mo (Fig. 4.3) alloys gave good fitting. The lattice parameters of both the compositions were almost same and the microstructure also showed single phase structure.



Fig.4.3. Rietveld plot for U-5at.%Mo as-cast. Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.

4.1.2 U-10 at.% Mo alloy

Microstructure of as-cast U-10 at.% Mo alloy (Fig. 4.4) consisted of single phase (average grain size 21 μ m) with small fraction of UO₂ inclusions. During the present

investigations, XRD analysis of 10 at.% alloy showed presence of monoclinic structure (α''), as given in Fig. 4.5. The XRD pattern showed that (131) line was split into (-131) and (131), of unequal intensities. This indicates that the γ -angle between 'a' and 'b' planes of the lattice is more than 90° [4.7], as discussed earlier. Stewart and Williams [4.13] have also reported lattice parameters of U-10 at.% Mo, water-quenched from 940° C, having γ -angle = 92.28°, a = 2.866 Å, b = 5.752 Å, c = 4.940 Å, taking C2₁/m space group. We have analyzed the monoclinic structure with Rietveld analysis taking P2₁/m space group setting [4.17] and lattice parameter obtained were as follows: β -angle = 126.68°, a = 3.27 Å, b = 4.95 Å, c = 3.15 Å. Though XRD pattern showed clear splitting of only one peak, (131), Rietveld analysis showed 3 pairs of split lines viz. (111), (112) or (131) (Fig. 4.6), as expected for monoclinic structure (α''). The equation for monoclinic structure is

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac} \right)$$

The last term in the equation shows that d spacing in monoclinic structures will be different for conjugate peaks.



Fig. 4.4 As-cast microstructure of U-10 at.% Mo shows single phase grains with oxide inclusions.



Fig. 4.5 XRD pattern of U-10 at.% Mo as-cast alloy clearly indicates the splitting of (-131) and (131) lines.



Fig. 4.6. Rietveld plot for U-10 at.% Mo as-cast alloy. Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.
4.1.3 U-33 at.% Mo alloy

The investigations of as-cast alloys with 33 at.% Mo were not reported in the literature. This is the composition of the alloy where only intermetallic compound is present in the system under equilibrium conditions. The present microstructural analysis of as-cast 33 at.% Mo alloys distinctly revealed dendritic microstructures with two types of dendritic morphology (Fig.4.7-4.8).



Fig. 4.7 As-cast microstructure U-33 at.% Mo at low mag. showing dendritic morphology.



Fig. 4.8 Dendritic microstructure observed in U-33 at.% Mo alloy in as-cast condition at 500 X. The Mo-dendrite is the darkest (indicated by no. 1), other dendrites are γ -(U) dendrites (indicated by no. 2) and matrix phase is indicated by no. 3.



Fig. 4.9 Higher magnification microstructure of as-cast alloy with 33 at.% Mo, to view 'Mo' rich dendrites as indicated by no. 1 in Fig.4.8.

Major fraction of dendrites was that of 'U' enriched dendrites, which were formed due to freezing of (γ - U) structure, seen as bright dendrites in Fig. 4.8. A small fraction of 'Mo' enriched equiaxed dendrites of grey colour were also observed, as seen in Fig. 4.8-4.9. The presence of these structures with different 'Mo' concentrations can be understood by assuming (i) equilibrium on the interface of different phases, (ii) complete diffusion in the liquid phase and (iii) almost negligible diffusion of atoms in solid phases. These assumptions are close to that of Scheil-Gulliver, and are reasonable for arc-melted samples, which are cooled by water-cooled copper hearth (~100°C/sec). The equiaxed dendrites precipitated out from the liquid alloy during non-equilibrium cooling, through L+ BCC (Mo) phase field. The grey colour dendrites (Fig. 4.8- 4.9) had almost equal short arms in three or four directions with 'Mo' content varying in the range of 83-95 at.% (Fig. 4.10).



Fig. 4.10 EDS spectrum (indicated with number 1 in Fig.4.8) taken on Mo rich dendrites in as-cast U-33 at.% Mo alloy.



Fig. 4.11 EDS spectrum of enveloping region (indicated with number 4 in Fig.4.8) in as-cast U-33 at.% Mo alloy shows 42.5 at.% 'Mo'.



Fig. 4.12 EDS spectrum of 'U' enriched dendrites (indicated with number 2 in Fig.4.8) in as-cast U-33 at.% Mo alloy indicates 34-40 at.% 'Mo'.



Fig. 4.13 EDS spectrum of matrix (number 3 in Fig.4.8) in as-cast U-33 at.% Mo alloy shows 24-27 at.% 'Mo'.

The surrounding region (number 4 in Fig.4.8) of these Mo dendrites has Mo content around 42.5 at.% (Fig.4.11) and as one move further, the Mo concentration reduces to 37 at.%. This envelope region is formed due to peritectic reaction between liquid phase and 'Mo' on the surface of Mo-dendrites (Liquid (29 at. % Mo) + BCC Mo $\rightarrow \gamma U$ (42 at. % Mo)). Sluggish diffusion rate in solid peritectic y-U phase (42 at.% Mo) on the surface of 'Mo' dendrites thwarts completion of peritectic reaction. Hence, significant amount of Mo dendrites are retained in the microstructure. This is the typical feature of peritectic reaction where the reaction product itself forms as an envelope and acts as a barrier for reaction to complete. As per the lever rule, even at the peritectic temperature (1284°C), the phase fraction of (Mo)dendrite does not exceed 7 % (at. %) for U-33 at.% alloy. In the as-cast microstructures of U -33 at.% Mo, area fraction of (Mo) dendrites was measured using IMAGE-J software and it was found to be ~5 % (vol %). Further cooling of the alloy below peritectic temperature resulted in precipitation of γ -U dendrites (No.2 in Fig.4.8) having composition 34-40 at.% Mo (Fig.4.12). After evolution of 'Mo' and γ -U phase containing higher 'Mo' than 33 at.% Mo, the remaining liquid phase was depleted of 'Mo' content. Hence, further cooling of the depleted liquid resulted in formation of residual γ -U (no.3 in Fig.4.8) containing 24-27 at.% Mo (Fig.4.13).

The most striking feature of these γ - U phase dendrites was the elongated morphology (bright colour) with secondary branching. The length of primary dendrites was in the range of 50-80 µm and width varied from 10 to 15 µm. The average size of the secondary arm length and width were 5-20 µm and ~ 5 µm respectively. The XRD pattern shown in Fig. 4.14, indicated presence of only γ - U phase in as-cast 33 at.% Mo alloy because the fraction of bcc-(Mo) dendrites was too low to be detected through XRD. The calculated lattice parameter of γ - U was found to be 3.3809 Å.



Fig. 4.14. Rietveld plot for U-33at.%Mo as-cast. Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.

4.2.4 EBSD Analysis Of U-33 at.% Mo Cast Alloy

Detailed EBSD analysis of as-cast microstructure, with 33 at.% Mo was carried out to know the orientation relation between different grains, as well as microsegregation in as-cast microstructure. EBSD inverse pole figure normal to the sample surface (IPF-Z) in cubic stereographic projection of as-cast U-33at.%Mo sample shows crystallographic orientations of different grains (Fig.4.15). Presence of different orientations (Fig.4.15) indicates absence of any preferred orientation. The band contrast image shows the dendritic morphology (Fig. 4.16). When the IPF-Z map of the microstructure is superimposed with band contrast, the superimposed map shows the dendritic micro-segregation pattern inside the grains along with orientations. Both types of dendrites (γ -(U) and (Mo)) are clearly revealed in bright contrast, when EDS count of Mo (L α line) is superimposed on IPF-Z with band contrast (Fig. 4.17). Mo-dendrite is brightest (Fig. 4.17, no.1), and remaining dendrites are γ -(U) dendrite (Fig. 4.17, no. 2). As the phase fraction of γ -(U) is high for 33 at.% U alloys, therefore, γ -(U) dendrites are observed in most of the grains. γ -(U) dendrite shows brighter contrast at the

centre of the grain, where Mo concentration is around 39-41 at.%, and darker contrast at the peripheral region of the grain having lower concentration of Mo (24.02 - 27.09 at.%).



Fig. 4.15 Inverse pole figure map (IPF-Z) of as-cast U-33at.%Mo. (The colour code represents orientation of grains along the z direction)



100µm

Fig. 4.16 Band Contrast map of as-cast U-33at.%Mo



Fig. 4.17 IPF- Z map superimposed with Band contrast and EDS count of as-cast U-33at.%Mo showing dendritic pattern along with micro-segregation. The Mo-dendrite is brightest (indicated by no.1), other dendrites are γ -(U) dendrite (indicated by no. 2).

4.2 Microstructure and phase analysis of annealed alloys

Microstructural features of annealed alloys were studied using optical microscope (OM) and scanning electron microscope (SEM).

4.2.1 U-2 at.% Mo alloy & U-5 at.% Mo alloy

After annealing, alloys with 2 and 5 at.%, Mo showed two phase lamellar microstructure (Fig. 4.18-4.19). In these alloys 'Mo' enrichment or phase-ordering were not

sufficient to designate the second phase as U₂Mo. As per the equilibrium phase diagram, alloys with 2 at.% Mo should have formed single phase α -(U), whereas, alloys with 5 at.% Mo should have undergone eutectoid reaction at 556 °C. That should have resulted in formation of α -(U) with ~4 at.% Mo and remaining small fraction of Mo should have formed U₂Mo. On further cooling, due to decrease in Mo in α -(U) some more fraction of Mo should tend to precipitate out from α -(U) and results in higher fraction of U₂Mo.



Fig. 4.18. Lamellar microstructure with dendrite of oxide was observed under SEM with dendrites in annealed U-2 at.% Mo alloy.



Fig. 4.19. Lamellar microstructure was observed along with oxide inclusions in annealed U-5 at.% Mo alloy.

However, reduced diffusion rate, at such low temperatures prevented formation of equilibrium U₂Mo phase even after annealing. Instead, it retained a non-equilibrium Mo rich phase along with α -(U) with significant amount of 'Mo' in matrix. Unless annealed for longer period just below the eutectoid temperatures, the small fraction of U₂Mo that might have formed after longer duration annealing in these low 'Mo' samples was not sufficient to be detected by XRD. Therefore, the XRD spectrum showed no characteristic U₂Mo peaks in 2 at.% and 5 at.% Mo samples (Fig. 4.20). XRD spectrum of only 5 at.% Mo sample, because XRD spectrum of 2 at.% and 5 at.% Mo alloys were indistinguishable. EDS analysis indicated presence of uranium oxide inclusions in these alloys.



Fig. 4.20. Rietveld plot for U-5at.%Mo annealed alloys showing only presence of orthorhombic α-(U). Dots are experimental scan, solid line is calculated pattern and bottom line is the residual plot.

4.2.2 U-10 at.% Mo alloy

The microstructure (Fig. 4.21) of annealed U-10 at.% Mo showed two different regions: lameller and non-lamellar.



Fig. 4.21. Lamellar microstructure, containing α -U+U₂Mo was observed in annealed U-10 at.% Mo alloys with increasing second phases.

According to TTT diagram given by Pedrosa et al., [4.21] U-10 at.% Mo alloys showed eutectoid transformation of γ phase into α and γ' (U₂Mo) phase after annealing. Similar results were reported by Pedrosa et al. [4.21] for U-Mo alloys and Hackenberg et al. [4.28] for U-Nb alloys. In the present study, XRD analysis of alloys containing 10 at.% Mo indicated the presence of (103), (112) peaks of U₂Mo intermetallic phase (Fig. 4.22) along with characteristic peaks of orthorhombic α -U. The volume fraction of U₂Mo in this alloy, calculated using Rietveld analysis of XRD spectrum, was around 22.2%. Hence the lamellar microstructure of annealed U-10 at.% Mo (Fig. 4.21) alloy has eutectoid decomposition product, α -U+U₂Mo. Pedrosa et al. [4.21] also reported similar phase composition for annealed alloys with 11.5 at.% Mo, however, they did not report the fraction of U₂Mo (γ') phase in their samples. Two small peak observed at 42.8° and 62.3°, may be formed due to oxide phase of UO_{2+x}.



Fig. 4.22. Rietveld plot for U-10at.% Mo annealed alloys showed presence of orthorhombic α and U₂Mo. Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.

4.2.3 U-33 at.% Mo alloy

U-33 at.% Mo annealed alloy showed a single phase microstructure with an average grain size of ~50 μ m (Fig. 4.23). XRD analysis of this alloy showed only U₂Mo phase (Fig. 4.24). Annealing treatment transformed γ -U phase of as-cast 33 at.% Mo alloy into an ordered compound (γ' - U₂Mo). Ordered γ' - U₂Mo phase has tetragonal structure with lattice parameters of 0.34 nm and 0.9991 nm. In U-33 at.% Mo the oxide phase is around 2.8%.



Fig.4.23 Single phase microstructure with small oxide inclusions in annealed U-33 at.% Mo alloy.



Fig. 4.24 Rietveld plot for U-33at.% Mo annealed alloys showing presence of U_2Mo . Dots are experimental scan, solid line is calculated pattern and bottom line is the residual curve.

4.3. Micro-hardness of U-Mo alloys

As-cast unalloyed uranium has hardness of HV 220, whereas, after homogenization at 625° C for 8 hrs. and vacuum cooling, the hardness reduced to HV 190. Hardness of as-cast 3.64 at.% Mo (1.54 wt.% Mo) alloy was HV 285 and after sufficient annealing no appreciable change in hardness took place [4.17]. In the present work, it was found that the annealed uranium-molybdenum alloys with 2 and 5 at.% Mo showed hardness in the range of HV 290-315. The hardness of these alloys increased with addition of 'Mo'. The U-10 at.% annealed alloy had hardness in the range of HV 401-424. However, annealed 33 at.% Mo alloy showed lower hardness of HV 385 compared to that of 10 at.% Mo. The variation of hardness profile with 'Mo' content in annealed U-Mo alloys is plotted in Fig. 4.25. The annealed alloys with 2 at.% and 5 at.% Mo were almost single phase, thus having low hardness. The slight increase in hardness with addition of 'Mo' from 2 at.% to 5 at.% was assigned to increase in rigidity of lattice structure by substitution of 'U' by small 'Mo' atoms in the lattice site of 'U'. However, considerable increase in hardness of alloy with 10 at.% Mo was assigned to the presence of higher amount of second phase as well as high Mo content. The alloy with 10 at.% Mo is a biphasic alloy as per XRD and microstructure analysis, with reasonable fraction of U₂Mo phase. The reduction in hardness for single phase U₂Mo compound with 33 at.% Mo, from the peak value may be due to reduced rigidity in microstructure in absence of second phase. Similar results were obtained by Pedrosa et al. [4.21] for the alloy with 21.61 at.% Mo, annealed at 500°C for 240 h. In microstructural analysis of this alloy, they observed a region 'C' that grew in size and phase fraction with increase in annealing time. This region was identified as acicular γ' and its hardness was found to be \sim 390 HV. In the same alloy, the regions with lamellar morphology, the hardness was ~ 450 HV. They have reported similar hardness for similar morphological regions for alloys with 11.55 and 15.73 at.% Mo, when annealed at 500°C for 240 hrs.



Fig. 4.25 Variation of hardness with Mo content (in at.%) in annealed U-Mo alloys, in Vicker's Scale using 300 gm load.

Pedrosa et al. carried out hardness measurements on individual grain within the alloy, therefore, they could measure the hardness for U₂Mo and (α + γ ') in the same alloy. Therefore, hardness values given by Pedrosa et al. are in reasonably good agreement with the present results. Their results also indicate that intermetallic compound (U₂Mo) has much higher hardness than α -(U) phase.

Sl. No.	Alloy	Crystal Lattice(Phases)	From RV Analysis (nm)
1	2 at.% as-cast	Orthorhombic (α -U)	a 0. 285, b 0.586,
			c 0.496
2	5 at.% as-cast	Orthorhombic (α -U)	a 0.285,b 0.586
			c 0.495
3	10 at.% as-cast	Monoclinic (a"-U)	a 0.326 ,b 0.496
			c 0.316
			β:126.69°
4	33 at.% as-cast	Cubic (γ-U)	a 0.338
5	5 at.% after	Orthorhombic (α -U)	a 0.285
	annealing		b 0.587
			c 0.496
6	10 at.% after annealing	Orthorhombic (α-U) + Tetragonal (U ₂ Mo)	Parameters for α -U phase
			a 0.286
			b 0.587
			c 0.497
			Parameters for U ₂ Mo phase
			a 0.343
			c 0.996
7	33 at.% after	Tetragonal (U ₂ Mo)	a 0.340
	annealing		c 0.999

Table 4.2: Lattice parameters obtained from Rietveld Analysis using MAUD program.

4.4 Summary

The U-Mo alloy is the candidate fuel for metallic fuelled fast rector. Fabrication of metallic fuel is carried out through injection casting and its microstructure evolve during

reactor operation due to thermal as well as irradiation effect. This emphasizes the importance of studying the as-cast alloy and annealed alloys.

The microstructure and phase analysis of four different U-Mo alloys have been investigated using OM, SEM-EDS and XRD in as-cast and as well as annealed conditions. The lattice parameters of the phases were determined through Rietveld analysis. The important findings are listed below:

- (a) U-2 at.% Mo and U-5 at.% Mo have similar microstructure in as-cast condition. Although the water quenched alloy has distorted orthorhombic alpha structure, but orthorhombic α -phase is present in as-cast alloy. The Rietveld analysis showed good fit and not much variation was observed in lattice parameter with change in Mo content in as-cast condition.
- (b) The monoclinic α'' phase was detected in as-cast U-10 at.% Mo alloy. The XRD pattern shows splitting of (131) line into ($\overline{1}31$) and (131) of unequal intensities confirming presence of monoclinic phase. The Rietveld analysis reveals three split lines viz. (111), (112) or (131).
- (c) The as-cast 33 at.% alloy showed presence of cubic γ -(U) phase with dendritic microstructure having secondary branching. The EDS analysis indicated micro segregation of 'Mo'. The microstructure also had a small fraction of bcc-(Mo) dendrites. The Rietveld plot shows good fit with cubic γ -U structure, with slight shrinkage in lattice parameter: 0.353 nm for pure γ -U and 0.338 nm for γ -(U) formed from as-cast alloy with 33 at.% Mo. EBSD analysis indicated absence of preferred orientation in as-cast structure as well as indicated dendritic pattern with microsegregation.

- (d) The annealed U-2 at.% Mo and U-5 at.% Mo alloys had orthorhombic α-U phase. Whereas, annealed U-10 at.% Mo had orthorhombic α-(U) phase and tetragonal U₂Mo phase. The Rietveld method quantified the volume percent of α-U and U₂Mo as 77.8 % and 22.2 %, respectively. The annealed U 33 at.% Mo has ordered U₂Mo intermetallic phase.
- (e) The Vickers Micro-hardness of annealed alloys increased with 'Mo' content due to the presence of two phase microstructure. Annealed single phase U-33 at.% Mo alloy shows reduced hardness than biphasic α -U+U₂Mo.

4.4 References

- 4.1 R.J. Van Thyne, D.J. McPherson, Trans. ASM 49(1957), 598-621.
- 4.2 G.H. Bannister and J.R. Murray, J. Less-Common Metall. 2(1960),372-382.
- 4.3 A.E. Dwight, J. Nucl. Mater. 2 (1) (1960), 81-87.
- 4.4 J. Lehmann, J. Nucl. Mater. 2(2)(1960), 152–168.
- 4.5 J. Lehmann, R.F. Hills., J. Nucl. Mater 3(1960), 261–268.
- 4.6 R.F Hills, B.R. Butcher, J.A. Heywood, J. Alloys Compd. 3 (1961), 155–169.
- 4.7 K. Tangri, G.I. Williams, J. Nucl. Mater. 4(2) (1901), 226-233.
- 4.8 R.L. Craik, D. Birch, C. Fizotti, F. Saraceno, J. Nucl. Mater. 6(1)(1962), 13–25.
- 4.9 B.W. Howlett, J. Nucl. Mater. 9(2) (1963), 143–154.
- 4.10 B.W. Howlett, J. Nucl. Mater. 35 (1970), 278–292.
- 4.11 G. Ostberg , M. Moller, B. Schonning-Christiansson. J. Nucl. Mater. 10(4)(1963), 329–338.

4.12 C.A.W. Peterson, W.J. Steele, S.L. DiGiallonardo, Report No. UCRL-7824, Livermore, California, August 1964.

4.13 D. Stewart, G.I. Williams, J. Nucl. Mater. 20(3) (1966) 262–268.

4.14 W.C. Erickson, G.E. Jaynes, D.J. Sandstrom, R. Seegmiller, J.M. Taub, Report No. LA-5002, September 1972.

4.15 M.K. Meyer, C.L. Trybus, G.L. Hofman, S.M. Frank, T.C. Wiencek, International meeting on reduced enrichment for research and test reactors, Jackson Hole, WY, Oct, 1997.

4.16 M.K. Meyer, J. Gan , J.F. Jue , D.D. Keiser , E. Perez , A. Robinson , D.M.Wachs, N. Woolstenhulme, G.L. Hofman , Y.S. Kim, Nucl. Eng. Tech. 46(2) (2014),169-182.

4.17 E. Dabush, J. Sariel, I. Dahan , G. Kimmel, Advances in X-ray Analysis 45 (2002),146-151.

4.18 D.E. Burkes, T. Hartmann, R.Prabhakaran, J-F Jue, J. Alloys Compd. 479 (2009) 140–147.

4.19 I. Tkach, N.-T.H. Kim-Ngan, S. Mašková, M. Dzevenko, L. Havela, A. Warren, C. Stitt, T. Scott, J. Alloys Compd. 534 (2012), 101–109.

4.20 N.-T.H. Kim-Ngana, I. Tkach, S. Mašková, A.P. Gonçalves, L. Havela, J. Alloys Compd. 580 (2013), 223–231.

4.21 T.A. Pedrosa, A.M. Matildes dos Santos , F.S. Lameiras , P.R. Cetlin, W.B. Ferraz,J. Nucl. Mater., 457 (2015) 100–117.

4.22 Development status of metallic, dispersion and non-oxide advanced and alternative fuels for power and research reactors, chapter 3, IAEA-TECDOC-1374, (2003).

4.23 J.T. Creasy, Thermal Properties of Uranium-Molybdenum alloys: Phase decomposition effects of heat treatments, Master Thesis, AM University of Texas, USA, 2011.

4.24 ASM International, ASM Handbook Volume 3: Alloy Phase Diagrams, 1992.

4.25 E.K. Halteman, Acta Cryst. 10 (1957), 166 -169.

4.26 A. Berche, N. Dupin, C. Guéneau, C. Rado, B. Sundman, J. C. Dumas, J. Nucl. Mater.
411 (1–3)(2011), 131–143.

4.27 X. Zhang, Y.F. Cui, G.L. Xu, W.J. Zhu, H.S. Liu, B.Y. Yin, Z.P. Jin, J. Nucl. Mater 402.

(2010) 15-24.

4.28 R.E Hackenberg, M.G. Emigh, AM. Kelly, P.A. Papin, R.T. Forsyth, T.J. Tuckr, K.D. Clarke, Report No. LA-UR-12-25218, Los Alamos National Laboratory, 2012.

Chapter 5: Study of Solidification Microstructure Evolution in U-Mo Alloy Through PFM

Injection casting of metallic fuel involve fast cooling of the melt, thus generating nonequilibrium conditions in liquid and solid phases. Fast cooling conditions are expected during casting of arc-melt alloys (~100 °C/s) [5.1]. Many authors [5.2] has simulated these cooling processes through Scheil-Gulliver model. However, phase field model is much advanced model than Scheil-Guilliver model for two reasons. Firstly, Scheil-Guilliver model assumes complete mixing in liquid phase (i.e. infinite diffusivity in liquid) and zero diffusivity in solid. However, in reality atoms in liquid and solid phase has finite diffusion coefficient and significant difference in diffusion rates exists in liquid and solid phase. Due to this, phase field model (PFM) assumes finite diffusivity in solid and liquid phase which is an huge improvement over Scheil-Gulliver model. Secondly, PFM takes into consideration the effect of interface which Scheil-Gulliver model fails to take into account.

Dendritic solidification is a multi-length scale pattern formation problem. For the last three decades it has been proven that the phase field technique is one of the advanced techniques to study dendritic crystal growth in meso-scale [5.3-5.10]. The growth of dendritic crystal is an interface dominated phenomena. In diffuse interface model, the interface is modelled as a mixture of parent and product phases. Thermal super-cooling and compositional super saturation in solid-liquid interface have pronounced effects on the growth process. Dendritic microstructure under non-equilibrium cooling can be formed under both low undercooling (≤ 1 °C) and high undercooling (≥ 100 °C) [5.3]. At high undercooling, dendritic tip velocity is in the range of 1-100 m/s. This velocity range comes in the domain of rapid solidification growth [5.4]. At low undercooling, the interface is considered to be in local

equilibrium condition. The local equilibrium condition ensures that the Gibbs-Thomson condition has been met and flux remains conserved across solid-liquid boundaries.

The main objective of this study is to understand the microstructural evolution of U-33at.% Mo during solidification and associated micro-segregation of Mo in dendritic microstructures during casting of U-Mo metallic fuel. Phase field modelling helps us to understand the effect of liquidus temperature, diffusivity, thermal conductivity, enthalpy of fusion, molar volume and other basic parameters of the system on micro-segregation and crystal growth processes. The present work is focused on interpretation of scanning electron microscopy (SEM) results along with energy dispersive spectroscopy (EDS) results of crystal growth during solidification of alloy (U- 33 at.% Mo) with the help of PFM. The evolution of γ -(U) and BCC-(Mo) dendrites has been studied with PFM and characterized using SEM along with EDS. The computational results calculated using Phase field model were compared with experimental results. The physical parameters used in the model for U-Mo system were taken from literature and are listed in Table 5.1 [5.11-5.18].

5.1 Phase Field model for Solidification

PFM applies a continuum field, *i.e.* a phase field characterized by a set of conserved (concentration (*c*) and temperature (*T*)) and non-conserved (crystal order-parameter (φ)) phase field variables. In the liquid-solid phase transformation, the continuously varying phase-field variable (φ) was taken as 0 in solid phase, 1 in liquid phase and changed from 0 to 1 at solid-liquid interface.

5.1.1 Entropy Functional

In the model [5.19], it has been considered that entropy of the system will be maximized during dendritic crystal growth. The entropy function (S) of an isotropic system

over volume 'V', which is a function of ' φ ', 'c' (concentration of Mo in U-Mo alloy) and 'e' (internal energy density which manifests as the temperature of the system), can be written as :

$$S = \int_{V} (s_b(\varphi, c, e) - \frac{\varepsilon_{\varphi}^2}{2} |\nabla \varphi|^2 - \frac{\varepsilon_{e}^2}{2} |\nabla c|^2 - \frac{\varepsilon_{e}^2}{2} |\nabla e|^2) \, \mathrm{d}V \tag{1a}$$

In the above equation (1), first integral expression ($s_b(\varphi, c, e)$) represents bulkentropy-density for bulk phases. The next three expressions represent gradient energy changes for phase-field-variables ' φ ', 'c' and 'e', respectively. The gradient coefficients, ε_{φ} , ε_c and ε_e are constant. To simplify these calculations some acceptable assumptions were made: (i) due to reasonable thermal conductivity of the metallic system, thermal gradient across the interface is negligible, so ε_e was ignored and (ii) in the narrow diffuse-interface region, concentration gradient was considered to be negligible, so ε_c was ignored. Hence the equation was reduced to the following form:

$$S = \int_{V} (s_{b}(\varphi, c, e) - \frac{\varepsilon_{\varphi}^{2}}{2} |\nabla \varphi|^{2}) \,\mathrm{dV}$$
(1b)

$$\frac{\delta S}{\delta \varphi} = \frac{\delta s_{\rm b}}{\delta \varphi} + \varepsilon_{\varphi}^{2} \nabla \varphi \tag{1c}$$

$$\frac{\delta s}{\delta c} = \frac{\delta s_b}{\delta c} \tag{1d}$$

$$\frac{\delta S}{\delta e} = \frac{\delta s_{b}}{\delta e} \tag{1e}$$

5.1.2 Evolution Equations

The evolution equation for the phase field non conservative phase field variable (φ) the evolution equation [5.19] is : $\dot{\varphi} = M_{\varphi} \frac{\delta S}{\delta \varphi} = M_{\varphi} (\frac{\partial s_b}{\partial \varphi} + \varepsilon_{\varphi}^2 \nabla \varphi)$ (2)

The interface mobility (M_{φ}) is a function of interface diffusivity. It is assumed that the interface mobility of individual atom depends on alloy composition, interface attachment coefficient and melting temperature of the elements. The model calculates interface mobility in the following way:

$$M_{\varphi} = (1-c)M^U + cM^{Mo} \tag{3}$$

$$M^{U/Mo} = \frac{(T_m^{U/Mo})^2 * \beta^{U/Mo}}{6\sqrt{2}L^{U/Mo}\delta},$$
(4)

Here, $M^{U/Mo}$ is the mobility of individual element, $L^{U/Mo}$ is the latent heats of fusion, δ is the phase field interface thickness, $\beta^{U/Mo}$ is the kinetic attachment coefficients and $T_m^{U/Mo}$ is the melting points of U and Mo respectively. The latent heat of fusion of U/Mo ($L_{U/Mo}^T$) is a function of temperature (eqn 5), whereas, other components are assumed to be independent of temperature.

$$L_{U/Mo}^{T} = L_{U/Mo}^{Tm} + \int_{T_{m}}^{T} (l_{P_{U/Mo}}^{L} - l_{P_{U/Mo}}^{s}) dT$$
(5)

The heat capacity of liquid phase is higher than that of solid phase $(l_{P,U/Mo}^{L} \ge l_{P,U/Mo}^{s})$. Therefore, the second term in eqn. (5) will be negative when T < T_m and positive when T>T_m. Due to high melting point of molybdenum, computational temperatures in the present work are lower than T_m^{Mo} , therefore, $L_{Mo}^T < L_{Mo}^{T_m}$. Moreover, on further cooling, the latent heat of Mo will continue to decrease. But, in case of uranium, both liquidus and peritectic temperatures are higher than T_m^U , therefore, $L_U^T > L_U^{T_m}$, but the latent heat difference of U and Mo decreases on cooling.

Evolution equations for conserved variables, concentration and internal energy are governed by normal conservation laws and are:

$$\dot{c} + \nabla J_c = 0 \tag{6}$$

$$\dot{e} + \nabla J_e = 0 \tag{7}$$

Where, J_c and J_e are concentration and energy flux.

$$J_{c} = M_{cc} \nabla \left(\frac{\delta s}{\delta c}\right) + M_{ce} \nabla \left(\frac{\delta s}{\delta e}\right)$$
(6a)
$$J_{e} = M_{ee} \nabla \left(\frac{\delta s}{\delta e}\right) + M_{ec} \nabla \left(\frac{\delta s}{\delta c}\right)$$
(7a)

 M_{cc} and M_{ee} are the mobility term for diffusion and heat conduction. M_{ce} and M_{ec} represent the cross effect between heat flow and diffusion and hence neglected. The gradient terms, $\nabla\left(\frac{\delta s}{\delta e}\right)$ and $\nabla\left(\frac{\delta s}{\delta c}\right)$ should be evaluated isothermally under fixed composition. Using eqn. 1d

and eqn.1e, equn. 6 and equn.7 become

$$\dot{c} = -\nabla J_c = -\nabla M_{cc} \nabla \left(\frac{\delta s_b}{\delta c}\right)$$
 (6b)

$$\dot{e} = -\nabla J_e = -\nabla M_{ee} \nabla \left(\frac{\delta s_b}{\delta e}\right)$$
 (7b)

 $g(\varphi)$ is a double well interpolation function of φ and can be represented by:

$$g(\varphi) = (\varphi^2 - 2\varphi^3 + \varphi^4) \tag{8}$$

Hence $g(\varphi)$ is maximum when φ is 0.5, i.e. at the interface location. It is zero at both $\varphi=1$ or 0.



Fig. 5.1 Double well interpolation function $g(\varphi)$.

The interpolation function $p(\varphi)$ can be represented by $p(\varphi) = \varphi^3 (10 - 15\varphi + 6\varphi^2)$ (9)



Fig. 5.2 Nature of interpolation function $p(\varphi)$, it is zero at $\varphi=0$ and 1 at $\varphi=1$.

Accordingly, the model for energy density for pure materials are:

$$e^{U/Mo}(T,\varphi) = e^{U/Mo,s}(T)(1-p(\varphi)) + e^{U/Mo,L}(T)p(\varphi)$$
(10)

Where, $e^{U/Mo,s}$ is energy densities for the U and Mo solid phases; and $e^{U/Mo,L}$ is energy densities for the U and Mo liquid phases.

$$ds_{U/Mo} = \frac{de_{U/Mo}}{T} \tag{11}$$

Integrating the above equation over temperature at constant ϕ ,

$$s_{U}(T,\varphi) = (1 - p(\varphi)) \int_{0}^{T} l_{U}^{s}(c) \frac{dT}{T} + p(\phi) \int_{0}^{T} l_{U}^{L}(c) \frac{dT}{T} + K_{U}(\phi)$$
(12)
$$s_{Mo}(T,\varphi) = (1 - p(\varphi)) \int_{0}^{T} l_{Mo}^{s}(c) \frac{dT}{T} + p(\phi) \int_{0}^{T} l_{Mo}^{L}(c) \frac{dT}{T} + K_{Mo}(\phi)$$
(13)

Where $l_{U/Mo}^{s}$ and $l_{U/Mo}^{L}$ are the specific heat of solid and liquid phase respectively and $K_{U/Mo}(\phi)$ is an integration constant. And $K_{U/Mo}(0) = K_{U/Mo}(1)$ according to the third law of thermodynamics.

For the case of a regular solution, the energy density can be written as

$$e(T,c,\varphi) = e_U(T,\varphi)(1-c) + e_{Mo}(T,\varphi)c + \Omega(\phi)c(1-c)$$
(14)

where $\Omega(\phi)$ is the regular solution parameter. Using eqn.10 in eqn.11, energy density and entropy of the solution will be

$$e(T, c, \varphi) = [(e^{U,s}(T)(1 - p(\varphi)) + e^{U,L}(T)p(\varphi)] * (1 - c) + [(e^{Mo,s}(T)(1 - p(\varphi)) + e^{Mo,L}(T))p(\varphi)] * c + \Omega(\phi)c(1 - c)$$
(15)

 $s_d(e(T,c,\varphi)) = s_U(T,\varphi)(1-c) + s_{Mo}(T,\varphi)c - \frac{R}{Vm}[c\ln(c) + (1-c)\ln(1-c)] \quad (16)$

Helmholz free energy density $f(T,c,\phi)$ can be constructed,

$$f(T, c, \phi) = e(T, c, \phi) - Ts_d(e(T, c, \phi), c, \phi)$$

= $f_U(T, \phi)(1 - c) + f_{Mo}(T, \phi)(1 - c) + \Omega(\phi)c(1 - c) + \frac{RT}{Vm}[c\ln(c) + (1 - c)\ln(1 - c)]$
(17)

where

$$f_{U/Mo}(T,\phi) = e^{U/Mo}(T,\phi) - Ts_{d,U/Mo}(T,\phi)$$
(18)

putting 10, 12 and 13 in eqn.18

$$f_{U/Mo}(T,\phi) = e^{U/Mo,s}(T)(1-p(\phi)) + e^{U/Mo,L}(T)p(\phi) - T * ((1-p(\phi))\int_0^T l_{U/Mo}^s(c)\frac{dT}{T} + p(\phi)\int_0^T l_{U/Mo}^L(c)\frac{dT}{T} + K_{U/Mo}(\phi))$$

$$= f_{U/Mo}^{s}(T,\varphi) * (1-p(\varphi)) + f_{U/Mo}^{L}(T,\varphi) * (p(\varphi)) - T * K_{U/Mo}(\varphi)$$
(19)

$$de = Tds - PdV$$

For a closed system (i.e. V=const.)

$$\frac{\partial s}{\partial e} = \frac{1}{T}$$

$$\nabla \frac{\partial s}{\partial e} = \nabla \frac{1}{T} = -\frac{1}{T^2} \nabla T \tag{20}$$

Again

$$\frac{\partial s}{\partial c_{e,\varphi}} = -\frac{1}{T} \frac{\partial e}{\partial c_{s,\varphi}} = -\frac{1}{T} \frac{\partial f}{\partial c_{T,\varphi}}$$
(21)

$$\frac{\partial s}{\partial \varphi_{e,c}} = \frac{1}{T} \frac{\partial e}{\partial \varphi_{s,c}} = \frac{1}{T} \frac{\partial f}{\partial \varphi_{T,c}}$$
(22)

$$\nabla \left(\frac{\delta s}{\delta c}\right)_{e,\varphi} = \frac{\partial}{\partial \varphi} \left(\frac{\delta s}{\delta c}\right)_{e,\varphi} \nabla \varphi + \frac{\partial}{\partial c} \left(\frac{\delta s}{\delta c}\right)_{e,\varphi} \nabla c = -\frac{1}{T} \frac{\partial^2}{\partial \varphi} \frac{f}{\partial c} - \frac{1}{T} \left(\frac{\partial^2 f}{\partial x^2}\right)_{T,\varphi}$$
(23)

Using eqns.20 and 23 the final evolution equations will be as follows.

$$\dot{\varphi} = M_{\varphi} \left[\epsilon^{2} \nabla^{2} \varphi - \frac{\partial}{\partial x} \left(\epsilon \dot{\epsilon} \frac{\partial \varphi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\epsilon \dot{\epsilon} \frac{\partial \varphi}{\partial x} \right) - W^{U} g'(\varphi) (1 - c) - 30 g(\varphi) L_{U} \left(\frac{1}{T} - \frac{1}{T_{m}^{U}} \right) (1 - c) - W^{Mo} g'(\varphi) c - 30 g(\varphi) L_{Mo} \left(\frac{1}{T} - \frac{1}{T_{m}^{Mo}} \right) c - \frac{1}{T} \frac{d\Omega}{d\varphi} c(1 - c) \right]$$

$$(24)$$

$$\dot{c} = \frac{1}{D_{L}} \nabla \cdot \frac{V_{m}}{R} c(1-c) D_{eff} \left[\left(\frac{R}{V_{m}} \frac{1}{c(1-c)} - \frac{2}{T} \Omega(\phi) \right) \nabla c + \left(\frac{1}{T} \frac{d\Omega}{d\phi} (1-2c) + W^{U} g'(\phi) + 30g(\phi) L_{U} \left(\frac{1}{T} - \frac{1}{T_{m}^{U}} \right) - W^{Mo} g'(\phi) - 30g(\phi) L_{Mo} \left(\frac{1}{T} - \frac{1}{T_{m}^{Mo}} \right) \right) \nabla \phi \right]$$
(25)

$$C\dot{T} = \nabla K \nabla T - 30 g(\phi) ((1 - c)L_U + cL_{Mo})\dot{\phi}$$
(26)

Whereas, $W^{U/Mo}$ are constants which represent energy humps at solid-liquid interface of pure U and Mo, and are given $\frac{3\sigma^{U/Mo}}{\sqrt{2}T_m^{U/Mo}\delta}$. *C*. is additive heat capacity and *K* is weight average

thermal conductivity of alloy and $\epsilon^2 = \frac{6\sqrt{2}L_{U/Mo}\delta}{T_m^{U/Mo}}$.

Diffusivities (D_s, D_L) and regular solution parameters (Ω_s, Ω_L) of the solid and liquid phases are combined with the interpolating function $p(\varphi)$ to form D_{eff} and $\Omega(\varphi)$ respectively,

$$D_{\rm eff} = D_s (1 - p(\varphi)) + D_L p(\varphi)$$
(27)

$$\Omega(\varphi) = \Omega_{\rm s}(1 - p(\varphi)) + \Omega_L p(\varphi) \tag{28}$$

The interface thickness (δ) for γ -(U) dendrite was assumed to be 1.1×10^{-8} m and for BCC-(Mo) dendrite it was 1.0×10^{-9} m.

$$\frac{\partial \Phi}{\partial \Gamma} = \left((\mathbf{1} - \mathbf{c}) \mathbf{M}_{\mathrm{A}} + \mathbf{u} \mathbf{M}_{\mathrm{B}} \right) * \frac{\mathrm{l}^{2}}{\mathrm{D}_{\mathrm{L}}} \frac{\mathrm{R}}{\mathrm{V}_{\mathrm{m}}} * \left[\widetilde{\nabla} \widetilde{\epsilon}^{2} \widetilde{\nabla} \phi - \frac{\partial}{\partial \widetilde{\mathbf{x}}} \left(\widetilde{\epsilon} \widetilde{\epsilon} \frac{\partial \Phi}{\partial \widetilde{\mathbf{y}}} \right) + \frac{\partial}{\partial \widetilde{\mathbf{y}}} \left(\widetilde{\epsilon} \widetilde{\epsilon} \frac{\partial \Phi}{\partial \widetilde{\mathbf{x}}} \right) - (\widetilde{W}^{A} g'(\phi) + 30g(\phi) \widetilde{L}_{A} \left(\frac{\mathrm{T}^{*}}{\widetilde{\mathrm{T}} \Delta \mathrm{T} + \mathrm{T}^{*}} - \frac{\mathrm{T}^{*}}{\mathrm{T}_{\mathrm{m}}^{\mathrm{A}}} \right) (\mathbf{1} - \mathbf{c}) - (\widetilde{W}^{B} g'(\phi) + 30g(\phi) \widetilde{L}_{B} \left(\frac{\mathrm{T}^{*}}{\widetilde{\mathrm{T}} \Delta \mathrm{T} + \mathrm{T}^{*}} - \frac{\mathrm{T}^{*}}{\mathrm{T}_{\mathrm{m}}^{\mathrm{B}}} \right)) \mathbf{c} - \frac{\mathrm{T}^{*}}{\widetilde{\mathrm{T}} \Delta \mathrm{T} + \mathrm{T}^{*}} \frac{\mathrm{d} \widetilde{\Omega}}{\mathrm{d} \phi} \mathrm{c} (1 - \mathrm{c})]$$

$$\dot{c} = \frac{1}{D_{L}} \nabla c(1-c) D_{c} \left[\left(\frac{1}{c(1-c)} - \frac{2}{T} T^{*} \tilde{\Omega} \right) \nabla c + \frac{T^{*}}{\widetilde{T} \Delta T + T^{*}} \frac{d\widetilde{\Omega}}{d\phi} (1-2c) \nabla \phi + \widetilde{W}^{A} g'(\phi) \right. \\ \left. + 30g(\phi) \widetilde{L}_{A} \left(\frac{T^{*}}{\widetilde{T} \Delta T + T^{*}} - \frac{T^{*}}{T_{m}^{A}} \right) - \left(\widetilde{W}^{B} g'(\phi) \right. \\ \left. + 30g(\phi) \widetilde{L}_{B} \left(\frac{T^{*}}{\widetilde{T} \Delta T + T^{*}} - \frac{T^{*}}{T_{m}^{B}} \right) \right]$$

$$\tilde{C}\frac{\partial\tilde{T}}{\partial\Gamma} = \tilde{\nabla}(\tilde{K})\tilde{\nabla}\tilde{T} - 30g\frac{T^*}{\Delta T}(\tilde{L}_{A} + \tilde{L}_{B})\frac{\partial\phi}{\partial\Gamma}$$

 \tilde{C} is the non-dimensionalised heat capacity and \tilde{K} is non-dimensionalised weight average thermal conductivity of alloy, \tilde{L}_A and \tilde{L}_B non-dimensionalised latent heat of fusion for U and Mo respectively.

5.1.3 Anisotropy in Interfacial Energy & attachment coefficient

Microscopic solvability theory has established that the magnitude of crystalline anisotropy affects dendritic crystal growth morphology, tip radius and tip velocity [5.20,5.21]. In this model anisotropic linear kinetic coefficient for interface attachment (β), surface energy and interface thickness (δ) have been considered. β takes care of attachment process at the solid-

liquid interface. It generates anisotropic mobility and relates moving front (planer or dendritic tip) velocity (V_n) with the under-cooling (ΔT) through the following relations:

$$V_n = \beta(\theta) \Delta T \tag{29}$$

$$\beta(\theta) = \beta_0(\theta)(1 - \epsilon_k \cos 4\theta) \tag{30}$$

where, $\beta_0(\theta)$ is the modulus of attachment coefficient, ϵ_k is the amplitude of kinetic attachment coefficient anisotropy and θ is $\arctan\left(\frac{\frac{\partial \varphi}{\partial y}}{\frac{\partial \varphi}{\partial x}}\right)$. The anisotropic surface energy (σ) is calculated from surface energy of the pure metals (σ_0) using

$$\sigma = \sigma_o (1 + \gamma \cos 4\theta) \tag{31}$$

where, γ is the strength of anisotropy. The γ has been taken equal to 0.05 in both the simulation. Coriell and Turnbull [5.22] have proposed the reduced crystal-melt interfacial tension through the equation, $\alpha_{U/Mo} = \left(\frac{N_o}{V_m}\right)^{1/3} \sigma_o/L$, where V_m is the molar volumes of pure U and Mo, N_o is the Avogadro's number, σ_0 is the surface free energy of pure elements and L is the latent heat of fusion. We have taken $\alpha = 0.427$ [5.23] for molybdenum. The value for U, which has bcc (A2) structure, is assumed be to equal. This value of α has been used for calculating the surface energy (σ_o) of U and Mo. It has been shown by Hoyt et al. [5.20, 5.21] that the kinetic parameter of anisotropy is almost one order of magnitude larger than the surface energy anisotropy and interface thickness anisotropy factor.

5.1.4 Finite element method & Initial microstructure

The evolution equations (eqn. 24-26) are solved by finite element method (FEM) using implicit time stepping and adaptive unstructured grid [5.19]. The use of the adaptive meshing

(Fig.5.3) significantly reduces computational load. A small nucleus of solid phase has been taken as equilibrated nucleus. The marginal stability analysis postulates that selective instabilities, created from stochastic noise at under-cooled solid liquid interface, grow into dendrite structure. However, recent theories postulate that the periodic oscillations at the interface are the results of interaction between shape and interfacial energy anisotropy [5.24]. Recent study [5.25, 5.26] indicates that even in the absence of any type of noise (mesh induce or additional thermal noise), side branching appears at high undercooling, supporting the deterministic model proposed by Glicksman.



Fig. 5.3 Adaptive meshing at the solid-liquid interface.

In the present simulation, for generation of secondary branch the stochastic noise dendrite has been introduced implicitly using random number generator. The size of the domain was 350 × 150 (in non-dimensional space) which ensures free dendritic growth. Tip temperature of the dendrites and tip position have been calculated considering, $\varphi = 0.5$. For both the cases non equilibrium cooling condition was created by assuming fixed temperature at the boundary. The input parameters for U and Mo are listed in Table 5.1.

Table 5.1 : Material parameters for the U-Mo system for simulation of γ and Mo rich dendrite.

Material property	Uranium		Molybdenum	
Molar heat capacity,	38.28	38.28 [5.11] at	34.28 at	35.54 at 1467 °C[5.11]
J.mol ⁻¹ K ⁻¹	[5.11] at	1467 °C	1284 °C	
	1284 °C		[5.11]	
Latent heat of fusion,	10.68 at	12.59[5.11] at	41.83at 1284	35.94[5.11] at1467 °C
kJ/mol	1284 °C	1467 °C	°C [5.11]	
	[5.11]			
Thermal conductivity,	75 at 1135 °C[5.12]		95 at 1284 °C [5.13]	
W/m.K				
Surface tension, J.m ⁻²	0.085		0.422	
Melting point, K	1408		2896	
Molar volume, m ³ /mol	9.418 X10 ⁻⁶		13.27 X10 ⁻⁶	
Linear kinetic	.0039		.0033	
coefficient for				
interface attachment,				
m/K/s				
Diffusivity (m ² /sec) in	10 ⁻⁹ at	10 ⁻⁸ at 1467 °C	10 ⁻⁹ at 1284	10 ⁻⁸ at 1467 °C
liquid state	1284 °C		°C	
	[5.14]			
Diffusivity (m ² /sec) in	$2*10^{-11}$ at	3.7*10 ⁻¹³ at 1467	$4*10^{-13}$ at	2.3*10 ⁻¹⁷ at 1467 °C
solid state	1284 °C	°C [5.16] in Mo	1284 °C	[5.18] in Mo lattice
	[5.15] in	lattice	[5.17] in U	
	U lattice		lattice	

5.2 (Mo)-dendrite Microstructure characterization and PFM simulation

Uranium has three allotropic forms viz. α (base centred orthorhombic), β (tetragonal) and γ (BCC) with a melting point of 1135 °C. Mo remains in BCC crystal structure up to its melting point at 2623 °C. Due to significant solubility of molybdenum in BCC- γ -(U) phase, the later gets stabilized to a wider temperature range. As seen from Fig.2.4, U-Mo melt with > 29 at.% Mo goes through a peritectic equilibrium at 1284 °C during cooling, liq. (29 at.% Mo) + (Mo) (99 at.% Mo) = γ -(U) (42 at.% Mo). The liquid alloys containing less than 28.7 at.% Mo, freeze to form γ -(U) phase. When liquid alloys containing 29-42 at.% Mo, are cooled, first BCC (Mo) phase precipitates out, which has ~0.9 at.% U. Further cooling results in peritectic reaction at 1284 °C, under equilibrium condition. Below this temperature the system has stable γ -(U) and liquid phases. The temperature of complete disappearance of liquid varies with original composition of the melt. The melt with 42 at.% Mo gets frozen into γ -(U) just below the peritectic temperature, 1284 °C. However, this is true only for very slow cooling of the melt, maintaining conditions of complete equilibrium. The high magnification SEM back scattered image of the equiaxed (Mo)-dendrites is given in Fig. 5.4 a. As per the phase diagram of U-Mo, these dendrites are the first solid phase formed during cooling from liquid melt. The (Mo) solid phase will remain in non-equilibrium state due to lower diffusion rates of elements in this phase at temperatures much below its melting point. Further cooling of the system resulted in precipitation of peritectic γ -(U) at 1284°C on the surface of (Mo) dendrite. Hence, the peritectic reaction did not complete during cooling. Alloys containing 29-42 at.% Mo are expected to be single phase γ -(U) below ~ 1200°C, as per equilibrium phase diagram. Due to non equilibrium cooling, resultant microstructure contained both γ -(U) and (Mo) phase. These (Mo)-dendrites have fourfold-symmetry and size of each dendritic arm was ~5-10 µm, with no secondary branches. Elemental X-ray map superimposed on back scattered electron (BSE) image showed presence of Mo and U (Fig.

5.4 b, c, d), which indicates higher concentration of molybdenum in (Mo)-dendrites compared to melt (33 at. % Mo). EDS analysis (Fig.5.4e) showed Mo concentration in the (Mo)-dendrites is 83 - 95 at.% (Table 5.2).

5.2.1 Evolution Of (Mo)-Dendrite & Validation Through EDS Analysis

To understand this evolution of Mo micro-segregation pattern in the (Mo)-dendrite, PFM simulation were done in a simulation box of 350×150 . The growth of dendritic structure has been simulated from an equilibrated Mo-rich nucleus drawn at the left side of the simulation box in axis-symmetric model. The rest of the simulation box was filled with U-33 at.% Mo melt. The equilibrated (Mo)-nucleus grows under the driving force of concentration and thermal gradient. The simulation were carried out with two different assumptions on diffusivity of uranium and molybdenum in liquid and solid phases: (i) *case 1*: diffusivities of Mo and U in solid phase (10^{-9} m²/sec) and in liquid phase (10^{-8} m²/sec) were assumed to be comparable and (ii) *case 2*: diffusivities of Mo and U in solid phase were 2.3×10^{-17} m²/sec and 3.7×10^{-13} m²/sec, respectively and in liquid phase both were 10^{-8} m²/sec. The experimental elemental image of the (Mo)-dendrite obtained in SEM is showing Fig. 5.5a. Detailed EDS analysis of (Mo)-dendrite shows that the Mo concentration at the midrib of dendrite is in the range of 90-94 at.% and in the periphery it is in the range of 83-87 at.%.









Mo La1



(c)



(d)



Fig. 5.4 (a) SEM image of (Mo)-dendrite, (b) EDS layered image having BSE image along with elemental X ray map of U and Mo, (c) & (d) Elemental X ray mapping image of U and Mo respectively, (e) Representative EDS profile taken on (Mo)-dendrite.

Location no.	at.% Mo from experimental EDS data	at.% Mo from PFM simulation
1	93	97
2	92	93
3	92	90
4	91	90
5	90	94
6	91	96
7	91	94
8	92	93
9	92	90
10	94	93
11	93	98
12	92	94
13	92	93
14	91	89
15	92	89
16	94	97
17	94	93
18	94	94
19	83	88
20	85	86
21	93	89
22	91	87
23	93	88
24	91	89

Table 5.2: El	DS analysis of	(Mo)- dendrite	(at.%).


Fig. 5.5 (a) Elemental X-ray map superimposed on SEM BSE image of (Mo)-dendrite with at.% Mo concentrations measured by EDS (Mo concentrations at different locations are given in Table 5.2), (b) Concentration map (mole fraction of Mo) of simulated Mo dendrite assuming $D_{U/Mo}=10^{-9}$ and $D_L=10^{-8}$ m²/sec (100 non-dimensional time step) at undercooling 20

Simulated microstructure of (Mo)-dendrite with comparable diffusivity of U/Mo in solid $(D_{U/Mo}^s = 10^{-9})$ and liquid $(D_{U/Mo}^L = 10^{-8})$ is shown in Fig. 5.5b (case 1). The concentration at the midrib is in the range of 90-98 at.% and at the periphery it is in the range of 81-85 at.%. For case-2, the mid-rib of the simulated microstructure of (Mo)-dendrite with significant difference in solid and liquid diffusivity ($D_U^s = 3.7 \times 10^{-13}$, $D_{M_0}^s = 2.3 \times 10^{-17}$, $D_{U/Mo}^{L} = 10^{-8}$), has the concentration of ~ 94 at.% Mo and the Mo concentration at some of the peripheral regions was as low as ~ 70 at.% Mo. It was found that calculated concentration of Mo in midrib region, based on assumptions of case-1 and case-2, match experimental observation. However, concentration at the periphery is in close agreement with the calculations carried out with assumptions of case-1. The calculated concentration of Mo in the peripheral region is much lower for *case-2* than experimental value. The reason may be, that in *case-2* much lower diffusivity of U and Mo was assumed in solid phase than in liquid phase, which lead to higher micro-segregation of Mo. This wider composition variation may be more relevant for cases where the diffusivity values of uranium ($D_{Mo}^U = 3.7 \times 10^{-13} \text{ m}^2/\text{sec}$) and molybdenum ($D_{Mo}^{Mo} = 2.3 \times 10^{-17} \text{ m}^2/\text{sec}$) are low. These experimental diffusivity values were determined by diffusion annealing method, in isothermal conditions, at high temperatures [Table 5.1]. In those experiments diffusivity only in single homogeneous phase measured. However, in the present experiments presence of the mushy zone which has two phase microstructure, gives more diffusion paths to the components than in single phase.

5.2.2 Tip-velocity of (Mo)-dendrite

In case of (Mo)-dendrites, variation of tip velocity with dimensionless time has been plotted in Fig. 5.6. The plot shows that for initial period, tip velocity is higher. Then it starts decreasing quickly and afterwards it drop offs very slowly. The calculated tip velocity is \sim 0.37-0.5 m/sec, which is slow enough to maintain local equilibrium at the interface.



Fig. 5.6 Tip-velocity of (Mo)-dendrite at different non-dimensional time

5.2.3 Variation of tip velocity with undercooling

The evolution of (Mo)-dendrite has been simulated at different undercooling, in the range of 5-60 °C. The change in tip velocity with undercooling has been plotted in Fig. 5.7. It has been found that the tip velocity increases with undercooling. According to the transition-state-theory, in case of low undercooling (<100 °C), the tip velocity (V_n) of dendrite is proportional to the undercooling (ΔT) and kinetic attachment coefficient (β). Therefore, tip velocity should increase with increase in undercooling, as observed during the present simulation. Tip temperature is an interplay between released latent heat during solidification and its diffusion in the cooler melt.



5.7 Plot of tip velocity vs. under-cooling for (Mo)-dendrite showing higher tip velocity at higher under-cooling.

5.2.4 Temperature profile of Mo dendrite during crystal growth

The temperature profile through the cut-line of a dendrite (Fig. 5.8a) has been plotted at different time of crystal growth (Fig. 5.8b). The cut-line is aligned with the midrib of solid dendrite. It starts from solid dendrite to some distance into the melt (Fig. 5.8a). Throughout the simulation, the temperature is kept fixed at the outer boundary (melt). Due to release of latent heat at the interface during crystal growth, the liquid just ahead of the solid liquid interface is at higher temperature compared to bulk molten metal. As a result, a negative temperature gradient is created from liquid just ahead of the solid-liquid interface to the bulk molten metal. The dendritic tip moves towards the cooler melt, which provides adequate driving force for dendritic growth. The plot (Fig.5.8b) shows that with time, the melt temperature increases. This increase in temperature is also very insignificant during solidification. In the present calculations, melt boundary is assumed to be far away from this solid-liquid interface region, thus its temperature is not affected by heat diffusion.



Fig.5.8(a) Cut-line drawn through the temperature field of Mo dendrite (The scale bar depicts the temperature in (°C) and (b) Plot of temperature profile through cut line of a (Mo)-dendrite at different non-dimensional time of crystal growth.

5.3 γ-(U)-dendrite Microstructure characterization and PFM simulation

The majority of dendrites seen in Fig. 4.7-4.8 are γ -(U)-dendrites, which are formed below peritectic temperature and have secondary branches. As the alloy was made from 33 at.% Mo melt, therefore, uranium rich melt is expected to have more crystals of γ -(U) phase than Mo dendrites. With decrease in cooling rate, the fraction of this phase is expected to increase, ~95 % of the bulk. The SEM image and elemental X ray maps with superimposed BSE image are given in Fig. 5.9 a, b, c and d respectively. EDS analysis (Fig. 5.9e) shows that in γ -(U)-dendrites, Mo concentration at the midrib of dendrite is in the range of 39-41 at.%. The matrix surrounding the dendrites has Mo concentration in the range of 24-27 at.%. Some fine precipitates of uranium rich phase are also seen in Fig. 5.9b, corresponding to the formation of small amount of uranium oxides.



Fig. 5.9(a) SEM image of γ-dendrite, (b) Elemental X ray image super imposed with BSE image of γ-dendrite, (c) Elemental X ray map of U shows high U enrichment in surrounding matrix, (d) Elemental X ray map of Mo shows high Mo enrichment at the centre of dendritic arm in γ-dendrite and (e) Representative EDS profile taken on γ-dendrite.

5.3.1 Evolution of (γ)-dendrite & Validation through EDS analysis

The simulation was also carried out to study the evolution of γ -(U)-dendrites at different undercooling, in the range of 5°C- 60°C. As the melt and the solid metal are especially good

conductor of heat, the variation of temperature will be very small with time and space. The simulation of γ -(U)-dendrite were carried out with 4×10^{-13} m²/sec and 2×10^{-11} m²/sec diffusivity of Mo and U in solid phase, respectively, and 10^{-9} m²/sec diffusivity of U and Mo in liquid phase.

The parametric study were also carried out by assuming equal diffusivity of U/Mo in solid and liquid phases, similar to the assumption made for (Mo) dendrites discussed in previous section. However, the computed concentration profile in the dendrite was found to be very different from the experimental observation. The reason for validity of lesser diffusion rates in case of simulation of γ -(U)-dendrites may be that this phase precipitates at lower temperature than (Mo). With decrease in temperature of the melt, the rate of cooling decreases, hence system moves towards equilibrium. Further, growth of secondary branches reduces tip velocity of γ -(U)-dendrites considerably compared to that of (Mo)-dendrite.

The concentration profile in simulated γ -(U) dendrite with unequal diffusivities in solid and liquid phases, given in Fig. 5.10 a, b, c and e at different time interval and were found to agree with experimental values (Fig. 5.10d).



Fig. 5.10 (a)-(c) Evolution of concentration field of U-Mo γ-(U) dendrites from pre-nucleated γ-(U) nucleus under non-isothermal condition at 100, 200 and 400 non-dimensional time step respectively. The simulation box size was 400x200 in non dimensional space, (d) The concentration of Mo (at.%) measured in EDS at respective position of γ-dendrites are given, (e) Evolution of U-Mo γ phase dendrites from pre-nucleated gamma nucleus at 500 non-dimensional time steps under non-isothermal condition.

The 2 to 4 order difference in diffusivity of U and Mo in solid phase and liquid phases generated the micro-segregation pattern as per the experimental observation. The simulation

showed that the γ -(U) dendrite started growing from the equilibrated nucleus in spherical shape, then under the influence of kinetic and interfacial anisotropy (interfacial energy and thickness), the spherical shape splits into different branches, maintaining four-fold symmetric condition. The concentration profile showed that the first solid had higher Mo concentration, thus melt got depleted of Mo. This is expected, because according to the phase diagram of U-Mo system, solid phase is richer in Mo than liquid phase, thus partition coefficient, $\frac{C_S^{Mo}}{C_r^{Mo}} > 1$. During simulation, it was found that after sufficient growth of primary branches, the surface of the dendrite started showing undulation, which later time grew into secondary branches. In Fig. 5.10e, the simulated image is compared with elemental X-ray mapped with overlapped BSE image (Fig.5.10d). The γ -(U) dendrite observed in SEM image had both primary and secondary branches. The EDS analysis showed micro-segregation in both primary and secondary branches. A comparison of SEM micrograph - EDS analysis with simulated dendrite shows that the structure and concentration profile of experimental results are matching closely with simulated dendrite. The Fig. 5.10d shows Mo concentration at the midrib of the primary branches are 40 at.% and at the periphery 27 at.%, in SEM-EDS image. The Fig. 5.10e shows that the simulated dendrite has Mo concentration at midrib 36-38 at.% and at periphery ~24 at.%. Another important feature of dendritic structure was the presence of entrapped liquid metal, depleted in Mo, between advancing dendritic arms, which solidified later. These entrapped liquid regions were also observed in simulated dendritic structure.

5.3.2 Tip-velocity of (γ)-dendrite

According to the theory of morphological stability [5.27], below the critical velocity of marginal stability, the perturbation may grow into dendrite. This theory assumes local equilibrium at the interface, which is very similar to our assumption. In Fig. 5.11, the tip

velocity of the growing dendritic crystal has been plotted with non-dimensional time. Higher tip velocity has been found for initial period. Then it drops off rapidly and then plateau out. This trend is similar to the observation made in case of (Mo)-dendrites, the calculated tip velocity of γ -(U) -dendrites is ~ 0.01-0.04 m/sec, which is much lower than the tip velocity calculated for (Mo)-dendrites, 0.37-0.39 m/sec.



Fig. 5.11 Tip-velocity of $(\gamma$ -U)-dendrite at different non-dimensional time (under-cooling 38

K).

5.3.3 Variation of tip velocity with undercooling

In Fig. 5.12 tip velocity has been plotted with undercooling, which shows that the tip velocity increases with increase in undercooling.



Fig. 5.12 Plot of tip velocity vs. under-cooling for (γ -U)-dendrite showing higher tip velocity at higher undercooling.

5.3.4 Temperature Profile Of γ Dendrite During Crystal Growth

The temperature distribution across the midrib of the dendrite has been plotted in Fig. 5.13. The temperature variation at the tip throughout the dendritic crystal growth simulation is very small (~0.25 °C). In a particular time instance the tip temperature is higher than the molten metal due to release of latent heat and negative temperature gradient is formed in the liquid. Two types of temperature distributions have been seen during simulation. Initially, during growth of primary branching tip temperature increased monotonically (up to ~300 dimensionless time step). However, subsequently secondary branch grew and heat release changed the temperature field in and around the tip region. This causes non-monotonic tip temperature distribution with time.



Fig. 5.13 Plot of temperature profile through cut line of a γ -(U) dendrite at different nondimensional times of crystal growth (tip of the curves represent solid-liquid interface).

After comparing experimental and simulated of Mo and γ -(U) dendrite, it is evident that the main morphological difference between the two types of dendrite is secondary branching. The cast structure forms during arc-melting has typically average cooling rate of the order of ~100 °C/s at high temperatures. The undercooling is a major parameter for dendritic growth. The solidification undercooling consists of four different types of undercooling. These are 1) kinetic undercooling, 2) curvature undercooling, 3) thermal undercooling and 4) constitutional undercooling. In our model, both types of dendrite were simulated in the similar range of undercooling. In the U-33at.% Mo alloy system, transformation temperature of Mo-dendrite is higher than γ -(U) dendrite. At higher transformation temperature (in case of Mo dendrite), due to high solute diffusivity in liquid phase, solute atoms get redistributed (causing more uniform distribution of Mo) faster than γ -(U) dendrite. This leads to higher

local constitutional undercooling for γ -(U) dendrite than Mo dendrite. So only primary stalk with no secondary branch develops in Mo dendrite. Whereas, γ -(U) dendrite, transforms at lower transformation temperature, develops into dendritic structure with secondary branches.

5.4 Summary

The microstructure of as-cast U-33 at. %Mo consists of two types of dendrites: equiaxed Morich B.C.C dendrite and γ -(U) dendrite with secondary branch. EBSD analysis indicates that these dendrites have no preferential orientations. SEM-EDS analysis shows considerable degree of microsegregation in both types of dendrites. The evolution of morphology and microsegregation of γ -(U) and (Mo) dendrite grown from the melt of U-33 at. % Mo have been simulated with WBM model based on phase field concept. Adaptive unstructured mesh has been used for the simulation. The important findings of the phase field modeling are listed below:

a. The detailed SEM-EDS analysis of equiaxed (Mo) dendrite shows midrib concentration 90-94 at.% and at periphery it is 83-87 at.%. The PFM simulation of (Mo)-dendrite shows similar concentration distribution assuming nearly equal U and Mo diffusivity in solid and liquid phase. The diffusivity in liquid phase is one order higher than solid diffusivity. The tip velocity of (Mo) dendrite has been calculated for range of undercooling. The tip velocity is found to be in the range of 0.3-0.4 m/sec and it increases with increasing undercooling. The tip temperature of dendrite rises during evolution process.

b. The microsegregation of γ -(U) dendrite has also been simulated at different undercooling. The simulated concentration profile matched very closely with experimental value when diffusivity of U and Mo in solid phase was assumed to be 4×10^{-13} and 2×10^{-11} m²/sec and in liquid was 10^{-9} m²/sec for U and Mo. The simulation shows increasing tip velocity with increasing undercooling. The tip temperature increases monotonically during growth of primary dendrites. After generation of secondary branch the tip temperature vary non-monotonically with time.

5.5 References

5.1 T. Velikanova, A. Bodar, L. Artyukh, O. Bilous, S. Firstov, D. Miracle: Titaniumboride composites: influence of alloying on constitution and properties of titanium-boride eutectic alloys, edited by O. N. Senkov, D. B. Miracle, S. A Fristov: Metallic Materials with High Structural Efficiency (Kluwer academic publishers, 2004), p. 260.

5.2 P Schaffnit, C. Stallybrass, J. Konrad, F. Stein, M. Weinberg: A Scheil–Gulliver model dedicated to the solidification of steel, CALPHAD 48, 184(2015).

5.3 E. J. Lavernia, T.S. Srivatsan: The rapid solidification processing of materials: science, principles, technology, advances, and applications, J.Mater.Sci., 45, 287 (2010).

5.4 M. Schwarz, C. B. Arnold, M. J. Aziz, D. M. Herlach: Dendritic growth velocity and diffusive speed in solidification undercooled dilute Ni-Zr melts: Mater. Sci. Eng. A 226-228, 420 (1997).

5.5 G. B. McFadden, A. A. Wheeler, R. J. Braun, S. R. Coriell, R. F. Sekerka: Phase-field models for anisotropic interfaces, Phys. Rev. E, 48, 3, 2016 (1993).

5.6 A. A. Wheeler, B. T. Murry, R. J. Schaefer: Computation of dendrites using a phase field model: Physica D, 66, 243(1993).

5.7 A. A. Wheeler, W. J. Boettinger, G. B. McFadden, Phase-field model of solute trapping during solidification: Phys. Rev. E, 47, 3, 1893(1993).

5.8 S. L. Wang, R. F. Sekerka, A. A. Wheeler, B. T. Murry, S. R. Coriell, R. J. Braun, G.B. McFadden: Thermodynamically-consistent phase field models for solidification, Physica D, 69, 189(1993).

5.9 W. J. Boettinger, A. A. Wheeler, B. T. Murry, G. B. McFadden: Prediction of solute trapping at high solidification rates using a diffuse interface phase-field theory of alloy solidification, Mater. Sci. Eng. A 178, 217 (1994).

5.10 W. J. Boettinger, J.A. Warren, Metall: Phase field method: simulation of alloy dendritic solidification during recalescence: Mater. Trans. A, 27A, 657 (1996).

5.11 A. T. Dinsdale: SGTE data for pure elements, Calphad 15, 317 (1991).

5.12 Thermophysical properties of materials for nuclear engineering, edited P.L. Kirikov,2006, p15.

5.13 Determining the thermophysical properties of molybdenum, by NETZSCH-Geratebau GmbH, 26th June 2013, on internet site: www.azom.com/article.aspx?ArticleID=9384, (accessed 12 November 2016).

5.14 Chemical engineering division research highlights: May 1962-April 1963, ANL-6766, Research reports, 38.

5.15 S. J Rothman: Diffusion In Uranium, Its Alloys And Compounds, 1961, ANL-5700, part C,

5.16 V. Palinov, A. I. Nakonechnikov, V. N. Bykov: Diffusion of Uranium in Molybdenum, Niobium, Zirconium and Titanium, Atomnaya Energiya,19(6), 521(1965).

5.17 Ke Huang, Dennis D. Keiser Jr., Yongho Sohn: Interdiffusion Intrinsic diffusion, atomic mobility, and vacancy wind Effect in c(bcc) Uranium-Molybdenum Alloy, Metall. Mater.Trans. A, 44A, 738 (2013).

5.18 J. Askill and D. H. Tomlin: Self-diffusion in molybdenum, Philos. Mag., 8: 90, 997(1963), doi=10.1080/14786436308214459.

5.19 Singer Loginova, H. M. Singer: The phase field technique for modeling multiphase materials: Rep. Prog. Phys.,71, 106501 (2008).

5.20 J. J. Hoyt, M. Asta, A. Karma: Atomistic and continuum modeling of dendritic solidification, Mater. Sci. Eng. R , 41, 121(2003).

5.21 J. J. Hoyt, M. Asta, A. Karma: Atomistic simulation methods for computing the kinetic coefficient in solid-liquid systems, Interface Sci. 10, 181(2002).

5.22 S. R. Coriell, D. Turnbull: Relative roles of heat transport and interface rearrangement rates in the rapid growth of crystals in undercooled melts, Acta. Metall. 30, 2135(1982).

5.23 B. Vinet, L. Magnusson, H. Fredriksson, P. J Desre: Correlations between surface and interface energies with respect to crystal nucleation, J. Coll. Int. Sci.255(4), 363 (2002).

5.24 M. E. Glicksman, J. S. Lowengrub, S. Li, Non-monotone temperature boundary conditions in dendritic growth, Modelling of Casting, Welding and Advanced Solidification Processing XI, www. math.uci.edu /~lowengrb /RESEARCH /publications /MCWASP XI 8MEG.pdf, (accessed 3rd December 2016).

5.25 M. E. Glicksman, Mechanism of Dendritic Branching, Metall. Mater. Trans A 43, 391(2012).

5.26 A. M. Mullis, Deterministic side-branching during thermal dendritic growth, Materials Science and Engineering 84, 012071(2015).

5.27 W. Mullins , R. Sekerka: Stability of a planar interface during solidification of a dilute binary alloy, J. Appl. Phys, 35, 444(1964).

Chapter 6 Fuel Clad Chemical Interaction of U-Mo Fast Reactor Fuel

Fuel clad chemical interaction is one of the major life-limiting phenomena for fast reactor metallic fuel. Presently, U-Pu-Zr is considered as a standard option for metallic fuel in fast reactor. Significant amount of post irradiation study has been carried out on U-10 wt.% Zr [6.1,6.2] and in U-Pu-Zr [6.3] to understand FCCI behaviour with Fe-based cladding. Initially, good FCCI performance of U-5 wt.% Fs (2.4 wt.% Mo, 1.9 wt.% Ru, 0.3 wt.% Rh, 0.2 wt.% Pd, 0.1 wt.% Zr, 0.01 wt.% Nb) driver fuel was observed in EBR-II [6.4]. This was attributed to the presence of Pd which combined with the lanthanide fission product during reactor operation and prevent the migration of fission products towards the clad. Based on this observation, Harp et al. [6.4] suggested addition of Pd (1-4 % as additive) in advanced U-10 Zr and U-Pu-Zr alloys to further mitigate FCCI. One of the main advantages of U-Pu-Zr metallic fuel reported in the literature is the presence of Zr rind outside fuel surface which prevents FCCI through raising the eutectic temperature [6.5]. A ZrN layer is also reported to be formed on the surface of fuel slug due to the presence of nitrogen at the surface. This ZrN layer prevents inter-diffusion of fuel and cladding constituents. However, ZrN layer losses its strength above 600 °C and totally redissolves in the fuel matrix at \sim 700 °C [6.6], thus it cannot protect the clad from FCCI at high temperatures and high power [6.3, 6.6-6.7].

There are many diffusion couple studies in U-Zr and U-Pu-Zr with stainless steel, ferritic steel and ferritic-martensitic clad materials. Ke Huang et al. [6.8] have investigated diffusion couple of U with Fe-15.95 at.% (15 wt.%) Cr alloy, in 600-700° C temperature range. Keisar et al. [6.9] and Lee et al. [6.10] observed formation of Zr rich layer at 700 °C in U-23Zr/HT9 diffusion couple, which was associated with the formation of Zr depleted α -U [6.10] upon cooling.

There is no data available in open literature on chemical interaction between U-33 at.% Mo and T91. Recently, some research work has been carried out on interaction of U-Mo alloys with pure Fe and Fe-Cr alloy [6.11, 6.12]. Nikitin et al.[6.12] have carried out diffusion couple experiments on U-22 at.% Mo (10 wt.% Mo) with pure Fe and Fe-12.79 at.% (12 wt.%) Cr, at 750 °C, for 5 hrs. Similarly, Aitkaliyeva et al. [6.11] have studied interaction between U-Pu-Mo and Fe-12.8 Cr alloy, at 700°C, for 75 hrs. In this chapter, results of diffusion couple (U-33 at.% Mo/T91) experiments at different isothermal temperatures (650 °C, 675°C and 700°C) will be discussed in details. The interaction zone microstructure between U-33Mo and T91 has been analysed with SEM-EDS and XRD.

6.1 Diffusion Couple Experiments

The layered structure evolved due to isothermal heating of diffusion couple is shown in Fig. 6.1. In general, after isothermal heating of U-33 at.% Mo/T91 diffusion couple, microstructures showed four distinct layers. These are marked as L1 to L4, starting from clad side. L1 layer has mainly U(Fe,Cr,Mo)₂ coexisting with smaller amount of uranium rich bright (θ) phase. The θ -phase is a phase with 50-60 at.% uranium and balance are T91 elements, Fe, Cr, Mo, almost in their constitutional compositions. Henceforth, U(Fe,Cr,Mo)₂ will be mentioned as UFe₂ and the layer will be called as UFe₂ layer (L1). In the diffusion couples experiments carried out at 700°C, for 15 days, L1-layer also had few dark precipitates (τ) containing ~55 at.% Fe , ~12 at.% Mo, balance uranium. L2 layer, is a thin U₆Fe layer located at the interface of clad and fuel-slug. Due to faster diffusion of uranium, Mo-autogenous layer (L3, >95 at.% Mo) was formed on the surface of slug region. L4 is another interaction layer in the slug that had lamellar structure. Phase analysis of this layer showed the presence of U₆Fe and Mo-rich phases (~96 at.% Mo) in lamellar morphology and very few patches of UFe₂ precipitates present close to Mo layer. After this lamellar L4 layer, un-reacted fuel slug having 33 at.% these diffusion couple experiments (Fig. 6.2). Thicknesses of the different layers formed during diffusion couple experiment are listed in Table 6.1. The average elemental compositions at different locations of the microstructures, determined by EDS analysis, are given in Table 6.2. To understand the fuel-clad interactions, the microstructure is divided into two zones, (i) clad-wastage zone (L1+L2) and (ii) slug-penetration zone (L3+L4). The evolution of microstructure in the diffusion couples heated at different temperatures for different time periods are discussed in the following sections.



Fig. 6.1. The microstructure in a U-33Mo/T91diffusion couple annealed at 700° C for 15 days. Gaps between red thick lines show average thickness of reaction layers. L1: $UFe_2+\theta+\tau$, L2: U₆Fe, L3: Mo-autogenous layer, L4: lamellar Mo+U₆Fe. (refer to the Table 6.2 for approximate composition of designated phases).



Fig. 6.2. XRD scan after 85 days of heating at 650°C.

Table 6.1 Thickness of different layers after annealing at different duration and phases present in the reaction layers

Zone	Phases (Layers)	Thk. (μm) 650 °C /14 d	Thk. (μm) 650° C /30 d	Thk. (μm) 650° C /85 d	Thk. (μm) 675 °C /7 d	Thk. (μm) 675 °C /14 d	Thk. (μm) 675 °C /40 d	Thk. (μm) 700 °C /3d	Thk. (μm) 700 °C /7d	Thk. (μm) 700 °C /15 d
Clad- wastage zone	UFe_2 (L1)	12	21	33	19	24	35	20	41	55
	U ₆ Fe (L2)	0.98- 1.0	.78-1.2	1-1.1	ND	0.84-1	0.9-1	ND	ND	0.8-1.2
Slug penetrati on zone	Mo- autogeno us layer (L3)	2	5	8	5	5	7	7	8	9
	Lamellar region (L4)	48	75	112	37	55	95	10	35	50

*ND= Continuous layer not detected

6.1.1 At 650°C for 14 days, 30 days and 85 days

The microstructure and elemental map of different elements of the diffusion couple along with line profile across the interaction layer, after 14 days annealing at 650°C, are given in Fig. 6.3a to 6.3i. L1 layer was formed due to initial diffusion of U from slug and its reaction with Fe, Cr and Mo from T91 clad and its average thickness was found to be 12 μ m. EDS analysis of L1 layer indicated the presence of θ (bright colour in back scattered SEM image) phase with high uranium content (~ 50-60 at. % U) towards slug side of the layer and relatively dull coloured phase (in Back scattered SEM image) of UFe₂ (33 at.% U) on the side of un-reacted clad. Apparently, Mo diffusion from the slug region into the clad was so low at temperatures < 700 °C, that molybdenum content of L1 layer remained almost same as that of T91. Thickness of U₆Fe layer (L2) in this diffusion couple was around 0.92 -1.08 μ m and that of Mo-autogenous layer (L3) was 2 μ m. The average thickness of lamellar-layer (L4) was 48 μ m and beyond that region, mostly un-reacted fuel slug containing 33 at.% Mo was found.

650 °C for 85 Days											
	Cr	Fe	Мо	U	Phase (in Layer)						
L1	6.3	58.7	0.8	34.2	UFe ₂						
	6.0	47.2	0.2	46.6	θ						
L2	1.5	5.3	1.9	91.3	U ₆ Fe in clad side						
L3	2.3	0.3	96.5	0.9	Mo-autogenous						
L4	0.0	14.5	1.1	84.4	Lamellar U ₆ Fe						
	0.9	1.2	91.4	6.5	Lamellar Mo						
675 °C for 40 days											
L1	5.3	53.0	0.6	39.1	UFe ₂						
	5.5	54.8	0.6	39.1	θ						
L2	1.2	12.1	0.8	85.9	U ₆ Fe in clad side						
L3	3.6	0.2	95.4	0.8	Мо						
L4	0	13.1	0	86.9	U ₆ Fe						
	0.0	0	92.5	7.5	Lamellar Mo						
700 °C for 15 days											
L1	5.5	59.7	1.2	33.6	UFe ₂						
	3.8	37.6	0.2	58.4	θ						
	3.8	46.5	12.2	37.5	τ						
L2	0.9	8.4	1.8	88.9	U ₆ Fe in clad side						
L3	2.3	0.3	96.8	0.6	Мо						
L4	0	14.1	1.6	84.3	U ₆ Fe						
	1.8	0.1	96.8	1.3	Lamellar Mo						

Table 6.2: EDS analysis of U-33Mo/T91 diffusion couples (at.%).







Fig. 6.3b EDS spectrum of bright region in UFe₂ layer in wt.% after 650°C 14 days annealing.



Fig. 6.3c EDS spectrum of dull region of UFe₂ layer in wt.% after 650°C 14 days annealing.



Fig. 6.3d EDS profile of Mo rich barrier layer after 650°C 14 days annealing.



Fig. 6.3e Elemental maps of different elements after 650°C 14 days annealing of the diffusion couple.



Fig. 6.3f Line profile across the interaction layer variation of composition across the different region after 650°C 14 days annealing.



Fig. 6.3g EDS profile of the bright region (U_6Fe) in the pellet side after 650°C 14 days annealing.



Fig. 6.3h EDS profile of dull phase in pellet side after 650°C 14 days annealing



Fig. 6.3i EDS profile of U-33 at.% Mo.

After annealing for 30 days, at 650°C, (i) UFe₂ layer (L1) was 21 μ m and (ii) U₆Fe layer (L2) was 0.8-1.3 μ m, therefore, there was no significant change in thickness of U₆Fe

layer. Clad-wastage layer grew due to growth of UFe₂ (L1) layer only. The average thickness of Mo-autogenous layer (L3) increased to \sim 5 µm. On the other hand thickness of lamellar-layer (L4) increased significantly to \sim 75 µm.

After annealing for 85 days, at 650°C, thickness of L1 layer became 33 μ m (Fig.6.4a-6.4d). L2 layer became more uniform, with thickness varying in the range, 1-1.1 μ m. Mo-autogenous layer (L3) grew to 8 μ m and the thickness of lamellar-layer (L4) was ~112 μ m.



Fig. 6.4a BSE of interaction layer formed after 85 days annealing at 650°C.



Fig. 6.4b. BSE image and EDS analysis of interaction layer after 85 days annealing at 650°C



Fig. 6.4c EDS layered image showing elemental mapping 85 days annealing at 650°C.



Fig. 6.4d: EDS spectrum of layer 3 after 650°C 85 days annealing.

6.1.2 At 675° C for 7 Days, 14 Days And 40 Days

At this temperature, morphology and trend of layer growth were similar to the observations made at 650 °C. Except U₆Fe (L2 layer), all layers grew with longer duration of annealing. The typical morphology of the interaction layers after 40 days of annealing at this temperature is given in Fig. 6.5.



Fig. 6.5 The interaction layer formed at 675°C after 40 days annealing.

6.1.3 At 700° C/ 3 days, 7 days and 15 days

After annealing for 3 days at 700°C, average thickness of L1 was 21 μ m. The thickness of Mo-autogenous layer (L3) varied from 6-8 μ m. The thickness of lamellar-layer (L4) in slug region was ~10 μ m (Fig.6.6), whereas, thickness of clad-wastage zone was 16-25 μ m. Composition of the L1 layer remained same as found after annealing at 650°C for different duration. The Mo-rich lamellar region (L4) had composition of Mo (87.7 at.%), Fe (2.6 at.%), Cr (2.2 at.%), U (7.5 at.%), whereas, Mo-autogenous layer (L3) at interfacial region had higher Mo content and lower uranium content than Mo-rich lamellar region (L4).



Fig. 6.6 Lamellar region formed in pellet after 3 days annealing at 700°C

With increase in annealing time, 7 days at 700°C, L1 thickness increased to 42 μ m and average thickness of clad-wastage zone was ~42 μ m. Mo-autogenous layer (L3) thickness increased to 8-9 μ m. EDS profile taken on this phase shows that Mo layer became enrich in Mo and depleted of U, Fe, Cr. The thickness of lamellar-layer (L4) was ~35 μ m. The composition of the two phases in lamellar region is given in Fig. 6.7a-d. Average thickness of interaction layer on clad side was ~42 μ m.



Fig. 6.7a BSE image showing the location from where EDS profile taken in the interaction layer after 7 days annealing at 700°C.



Fig. 6.7b EDS profile of Mo rich barrier layer after annealing at 700°C for 7 days.



Fig. 6.7c EDS profile taken on U₆Fe after annealing at 700°C for 7 days. (U 83.30at.%, Mo 1.61 at.%, Fe 14.64 at.%, Cr 0.46 at.%).



Fig. 6.7d EDS profile of Mo rich lamellar region after annealing at 700°C for 7 days.

With further annealing for 15 days at 700°C, L1 layer had additional precipitates of τ (\approx Fe _{0.55} Mo _{0.12} U _{0.33}) along with (UFe₂+ θ) (Fig. 6.8a). EDS data of the phases are given in Table 6.2. The layer thickness of L1 was 55µm and EDS layered image of the diffusion couple along with individual elemental map is given in Fig. 6.8b. The L2 layer thickness was same as ~1 µm. The thickness of adjacent Mo-autogenous layer (L3) became uniform (~8 µm) and composition remained same. The thickness of lamellar-layer (L4) in the slug was 50 µm. The U–depleted, Mo-rich phase of lamellar layer had become further enrich with Mo (Mo 96.8 at.%, U 1.3 at.%, Cr 1.8 at.%, Fe 0.1 at.%) (Fig. 6.8c). XRD analysis confirmed presence of U₆Fe, UFe₂ phase (Fig. 6.8d) along with γ -U and bcc Fe matrix. Thickness of slug-penetration zone is ~ 2-3 times that of clad-wastage zone at 650 °C and 675 °C, whereas, at 700 °C it is 0.5-0.8. The EDS profile of τ phase within L1 layer is given in Fig. 6.8e.



Fig. 6.8a BSE image of interaction layer after annealing at 700°C for 15 days.



Fig. 6.8b Elemental maps of elements after 700°C 15 days annealing of the diffusion couple.


Fig. 6.8c EDS profile of Mo rich region in the lamellar structure after annealing at 700°C for 15 days.



Fig. 6.8d XRD scan after 700°C 15 days annealing of the diffusion couple.



Fig. 6.8e EDS profile of τ phase within L1 layer, after annealing at 700°C for 15 days.

6.2 Discussions

The evolution of microstructures during diffusion couple experiment is in the realm of reaction-diffusion system. There are two processes: (1) diffusion of atoms of reactants from bulk in opposite directions due to concentration gradient and (2) chemical reactions at the interface. Unlike the homogeneous reaction, in this case, the interaction products remain at the interface and are not removed from the reaction site, thus separating the reacting phases from each other. The thermodynamic stability of the product phases and diffusion rates of the reacting elements through the product phases control the kinetics of layer growth. The effects of temperature and time on the clad-wastage zone and slug-penetration zone are discussed in detail in the following sections.

To understand the fuel-clad interactions, the microstructure is divided into two zones, (i) clad wastage zone and (ii) slug penetration zone. The different layers formed in U- 33Mo/T91 couple have been listed in Table 6.3. The effects of temperature and time on

these zones are discussed in detail in the following sections.

Table 6.3 . The comparison between U-23Zr/Fe-12Cr and U-33Mo/T91 interaction layer
formation at 700 °C

	U-33Mo/T91 [This work] at 700 °C	U-23Zr/Fe-12Cr [6.13] at 700 °C
Unreacted	Solid solution of T91	Solid solution of Fe-Cr
Clad		
Clad-	1. UFe ₂ + θ (~ 50-60 at. % U;50-40	1. Cr-rich layer
Wastage	at.% Fe+Cr)+ τ (Fe 46.6 at.%;	2. UFe ₂ (<3 at% Zr+ \sim 10% Cr)
Zone	Mo 12 at.%; Cr 4 at.%; U 37.4	3. $U_6Fe (<2 at\% Zr+1\% Cr)$
	at.%)	4. U ₆ Fe+ZrFe ₂ (~10%Cr+~10-20
	2. U ₆ Fe	%Cr)
Slug	3. Mo autogenous layer	5. $U_6Fe+\chi(\sim 3\% Cr) (U-32Zr-50Fe)$
Penetration	4. Lamellar U_6Fe+ Mo rich phase	[6.14]
Zone		6. $U_6Fe+\epsilon$ (U-(33-50)Zr-33Fe)
		[6.14]
		7. β-U+ε
		8. $\gamma_1 + \lambda$ (U-(21-25)Zr-6Fe) [6.14]
Unreacted	U-Mo solid solution	γ1+γ2
Fuel		

6.2.1 Clad wastage zone (L1 and L2)

The L1 and L2 layers were present in the clad-wastage zone of U-33 at. %Mo/T91 diffusion couple. UFe₂ layer formation has been reported by Ke Huang et al. [6.8] in diffusion couple experiment of U with Fe-16 at.% Cr alloy, at 600-700 °C temperature range. The clad-wastage zone of U-23 at.% Zr /Fe-12 at.% Cr diffusion couple reported by Nakamura et. al [6.13] consisted of four layers (Table 6.3), (i) Cr-rich layer, (ii) UFe₂ (<3 at.% Zr+~10 at.% Cr), (iii) U₆Fe (<2 at.% Zr+1 at.% Cr) and (iv) U₆Fe+ZrFe₂. The striking differences between the present U-33Mo/T91 and reported U-23Zr/Fe-12Cr diffusion couples are: (a) absence of Cr-rich layer near un-reacted clad zone, (b) absence of U₆Fe +ZrFe₂ layer and (c) much thinner U₆Fe layer (L2) in clad-wastage zone observed in the present studies (Table 6.3). The Cr-rich layer was also seen by other authors in U/ Fe-16 at.% Cr [6.8]

diffusion couples. The poor solubility of Cr in U_6 Fe phase [6.8] leads to accumulation of Cr at the clad side in high Cr alloys. The slightly reduced Cr content in T91 and lesser diffusion of Fe from clad (due to the presence of Mo-autogenous layer) in the present diffusion couple study may be responsible for the absence of Cr rich layer at the clad side.

Fe and U form very stable intermetallic compounds, UFe₂ ($\Delta_f G^\circ = -22565.2$ J/atom at 700°C) and U₆Fe ($\Delta_f G^\circ$ = -8805 J/atom at 700°C), which provide strong driving force for their diffusion from one region to another in U-33 at.% Mo/T91(9 Cr-1Mo) diffusion couple experiments. Cr does not react with uranium to form any intermetallic compound. Whereas, Mo can form weak compounds with Fe (μ -Fe₇Mo₆ and λ -Fe₂Mo). The solubility of Mo in bcc- Fe \approx 2.5 at.% at 700°C [6.15], but < 1 at.% Fe [6.15] and < 1 at.% uranium can dissolve in bcc-Mo lattice at the same temperature. Very low solubility of U and Fe in Mo results in constrained diffusion of these elements through autogenous Mo-layer. On immediate contact of U-33 at.% Mo with T91 clad, uranium reacts with Fe of T91 and forms U₆Fe and UFe₂. Once U_6Fe and UFe_2 layers form, subsequently reaction is possible only when the reacting element diffuse through these product interaction layers, U_6Fe (L2) and UFe₂ (L1) for further reactions. Mo has poor solubility in U_6Fe (L2) and UFe_2 (L1), hence diffusion of Mo towards the clad through these phases is restricted. Moreover there is no chemical driving force for Mo to move either from fuel to clad or from clad to fuel, as it is an alloying element in both and doesn't form very strong compound with either of them. Hence accumulation of Mo at the fuel side takes place, resulting in the formation of Mo-layer (L3). As sufficient Mo could not reach in the clad side, $\mu(Fe_7Mo_6)$ and $\lambda(Fe_2Mo)$ phase formation did not take place. After formation of autogenous Mo-layer, U from slug had to diffuse through (i) autogenous Molayer (L3) (ii) U₆Fe-layer (L2) and (iii) UFe₂-layer (L1) to reach clad, thus retarding further interaction of fuel and clad. Elemental Mo has higher melting point and higher thermal

conductivity (~4-5 times than U and Zr), hence formation of this autogenous-Mo layer surrounding the slug may not hinder the heat transfer during reactor operation.

For the growth of U_6Fe (L2) in clad side, sufficient uranium atoms must diffuse through Mo-autogenous layer to reach T91. From the experimental observation it was found that a very thin (1 µm) U_6Fe layer (L2) was formed in clad-wastage zone, which did not grow even during long period of annealing at 650°C and 700°C (Table 6.1). In contrast to this, in U-23Zr/Fe-12Cr diffusion couples, appreciable ZrFe₂ and U_6Fe layers formed along with UFe₂ in the clad-wastage zone (6.13, Table 6.3) indicating that a good amount of uranium could diffuse through these intermediate layers. Hence the rate determining step of fuel-clad interaction of U-33 at.% Mo-T91 diffusion couple is diffusion of uranium through Moautogenous layer.

As the rate determining step in the reaction of uranium with iron is diffusion of uranium through autogenous Mo layer, the amount that diffuses through this Mo-layer quickly diffuses through U₆Fe layer and forms UFe₂. Therefore in the clad side there is always limited supply of "U" resulting in very thin U₆Fe layer (L2). But it may be enough for the formation of UFe₂ and 50-60 at.% uranium rich θ phase at the clad side. As the diffusion of U through U₆Fe is faster than that in Mo-autogenous layer (Table 6.4), therefore, most of the diffused uranium is consumed in forming UFe₂ compound and 50-60 at.% uranium rich θ phase clad-wastage region. This explains lack of growth of thin U₆Fe-layer (L2), whereas, reasonable growth of UFe₂-layer (L1) with time. Pavlinov et al. have shown higher diffusivity of uranium in γ -uranium and γ -(U, Mo) are substantially higher than that in Mo lattice (Table 6.4). These diffusivity data indicate that the presence of autogenous-Mo layer at the slug surface can retard free diffusion of U atoms significantly into the clad and reduce clad-wastage.

Diffusing	Matrix	Do	Activation	D	Reference
element		(m^2/sec)	Energy	(m^2/sec) (Temperature	
		``´´´	(KJ/mol)	Range, °C)	
U	γ-U	1.12×10 ⁻⁷	110.9	NA	[6.17]
U	γ - U, Mo	2.5×10 ⁻⁷	135.9	NA	[6.18]
Fe	U	3.06×10 ⁻¹⁷	50.2	9.50×10 ⁻¹¹ -2.26×10 ⁻¹⁰	[6.19]
				(786.9-989.6)	
Fe	Mo	0.15×10 ⁻⁴	346.0	$1.06 \times 10^{-19} - 1.15 \times 10^{-16}$	[6.20]
				(1000-1350)	
U	Mo	7.6×10 ⁻⁷	318.0	$2.0 \times 10^{-16} - 3.0 \times 10^{-14}$	[6.16]
				(1500-2000)	
U	U ₆ Fe	NA	375	$0.0162 \times 10^{-16} - 1.28 \times 10^{-16}$	[6.21]
				(575-650)	

Table 6.4 . Diffusivity Parameters obtained from literature

6.3.2 Slug Penetration Zone (L3, L4)

For growth of lamellar layer in the slug, Fe atoms diffused through UFe₂ (L1), U₆Fe (L2) and Mo-autogenous layer (L3) layers and penetrated into the slug. In the slug area, reaction of U with Fe gave rise to the formation of lamellar morphology of U₆Fe and Mo (L4) through cellular precipitation type reaction and beyond that un-reacted fuel was present. In cellular precipitation one of the products has similar crystal structure (bcc) as parent phase with different composition (\approx 96 at.% Mo) than parent phase (33 at.% Mo).

U-Mo(bcc)+Fe \longrightarrow U₆Fe(tetragonal)+Mo (bcc)

Here, the diffusion of Mo occurred across the cellular boundary, and hence there may be a compositional gradient along the precipitate in thickness direction. The growth of this lamellar layer is preceded by diffusion of Fe in this region.

Due to strong Fe- vacancy binding energy, along with a high degree of correlation between the directions of successive vacancy jumps, Fe diffuses very fast through γ -U, whereas, diffusivity of Fe in bcc-Mo is significantly less (Table 6.4). Hence formation of the autogenous Mo layer (L3) in present diffusion couple experiments significantly retards diffusion of Fe towards slug side, hence, retarding growth of this lamellar layer (L4) in slug side.

U/Fe-Cr diffusion couple had only U₆Fe phase in slug penetration side [6.8], whereas, U-23Zr/Fe-Cr couple had multiple layers in slug penetration area [6.13, 6.14]. Nikitin et al. [6.12] have also studied diffusion couple of U-22 at.% Mo with Fe and Fe-Cr at 750 °C. They observed formation of UFe₂ in clad zone and U₆Fe in fuel zone; however, they did not report formation of a separate Mo-rich layer. The higher Mo content in our slug material (U-33 at.% Mo) might have lead to the formation of the Mo rich layer surrounding the slug material in the temperature region 650-700°C.

After formation of autogenous Mo-layer, U from slug had to diffuse through (i) autogenous Mo-layer (L3) (ii) U₆Fe-layer (L2) and (iii) UFe₂-layer (L1) to reach clad, thus retarding further interaction of fuel and clad. The U has very low solubility (~1 at%) in Mo and diffusivity of U in Mo is also very low $(2.0 \times 10^{-16} - 3.0 \times 10^{-14} \text{ m}^2/\text{sec} (1500-2000 ^{\circ}\text{C}))$, therefore, Mo-layer act as diffusion barrier for uranium.

6.2.3 Diffusion Path In Ternary U-Mo-Fe

To understand diffusion paths of elements in U-33 Mo/T91, we simplified the system as U-33Mo/Fe-1Mo. The U-Mo-Fe ternary phase diagram was calculated using optimized binary interaction parameters reported in literature U-Mo [6.22], Mo-Fe [6.23] and U-Fe [6.24]. The phases observed in the interaction zones were compared with U-Mo-Fe isothermal at 700 °C (Fig.6.7). The diffusion paths of the elements were drawn on this isothermal section by a blue dotted line (Fig.6.7). In the (U-33 Mo)-T91 diffusion couple, the fuel is γ -(U, 33 at.% Mo) (Fig. 6.7, Point E) coupled with clad of composition, Fe-0.6% Mo (Fig. 6.7, Point A). The system cannot achieve equilibrium at such low temperature in limited

time span, therefore, thermodynamic driving forces constraint by diffusion of elements results in appearances of different phases. In Fig. 6.9, the clad composition is represented as Point-A and slug composition is represented as Point-E. The average compositions of the intermediate layers were as follows: Point-B (L1+L2): U_{39} -(Fe,Cr)₅₉-Mo₁, Point-C (L3): U_{2} -(Fe,Cr)₂-Mo₉₆, Point-D: U_{84} -(Fe)₁₅-Mo₁. The U_6 Fe+Mo layer (L4) is a non-equilibrium region between two extreme phases, Point-C and Point-D. In this diagram, Point-B and Point-C correspond to the average compositions of L1+L2 and L3 layers, respectively.



Fig. 6.9: Calculated phase diagram of U-Mo-Fe and calculated diffusion path. A: Fe Clad, B: U₃₉-(Fe,Cr)₅₉-Mo₁, C: U₂-(Fe,Cr)₂-Mo₉₆, D: U₆Fe, E: Slug (U-33 at.%Mo).

6.2.4 Calculation Of Growth Rate

The growth constant (K_p) for clad-wastage zone (L1+L2) (major phase UFe₂), lamellar-layer (L4) and slug-penetration zone (L3+L4) were calculated (Fig.6.10 and Table 6.5) assuming parabolic diffusion mechanism. The activation energies of layers were calculated (Table 6.5) using Arrhenius equation $(K_p = K_0 e^{-\frac{Q}{(R*T)}})$, where Q is the activation energy in J/mol, T is the temperature in Kelvin and R is the universal gas constant (J/mol/K). The parabolic growth rate of slug-penetration zone (L3+L4) and clad-wastage zone (L1+L2) in U-33 at.% Mo/T91 diffusion couple experiments are compared with U/Fe-16 at.% Cr diffusion couple in Table 6.5. At 700 °C, the growth rate of U₆Fe (L4) layer in U-33 at.% Mo/T91 was found to be 10.48×10^{-16} m²/sec, whereas, for U/Fe-16 at.% Cr alloy, Huang [6.8] reported it to be 21.02×10^{-15} m²/sec . The growth rate of UFe₂ (L1) layer in U-33 at.% Mo/T91 (12.75 × 10⁻¹⁶ m²/sec) was found to be comparable with that in U/Fe-16 at.% Cr alloy (7.11×10⁻¹⁶ m²/sec). Significantly lower growth rate of lamellar-layer in U-33 at.% Mo/T91 than in U/Fe-16 at.% Cr may be attributed to lower diffusion of Fe through Mo-autogenous layer (Table 6.5).



Fig.6.10:Thickness² vs time plot at three Time (Sec) different temperatures for growth study of clad wastage layer (CWL) (L1+L2), slug penetration layer (SPL) (L3+L4) and Mo (L3) layer .

Similar observation was made at 650°C, where, growth rate of clad wastage zone in U-33 at.% Mo/T91 couple $(7.90 \times 10^{-17} \text{ m}^2/\text{sec})$ is comparable with its growth rate in U/Fe-16 at.% Cr couple $(5.30 \times 10^{-17} \text{ m}^2/\text{sec})$ [6.8] and in U/(single crystal)-Fe $(3.06 \times 10^{-17} \text{ m}^2/\text{sec})$ [6.25]. However, growth rate of clad-wastage zone (UFe₂+U₆Fe+ZrFe₂) of U-23Zr/Fe diffusion couple was $8.0 \times 10^{-16} \text{ m}^2/\text{sec}$ [6.21], which is one order higher than in U-33 at.% Mo/T91 (L1+L2). Growth rate of slug-penetration zone (L3+L4) of U-33 at.% Mo/T91 is also one order less compared to that of U-23Zr/Fe couple (Table 6.5). At 650°C, the growth rate of U₆Fe in lamellar layer (L4) in U-33 at.% Mo/T91 couple is ~ 5 times lower than that in U/Fe-16 at.% Cr. At 700 °C, the growth rate of this layer in U-33 at.% Mo/T91 was ~ 20 times lower than in U/Fe-16 at.% Cr. Hence, clad wastage and slug penetration region are much lesser in U-33 at.% Mo/T91 diffusion couple compared to U-23Zr/Fe, U-23Zr/Fe- 12at.% Cr and U/Fe-16 at.% Cr diffusion couples.

The total interaction zone (L1+L2+L3+L4) thickness and growth rate at different temperatures are also listed in Table 6.6. It was observed that the growth rate of interaction zone in U-33Mo/T91 increased with increase in temperature. In Fig. 6.11, the interaction zone growth rate of U-33Mo/T91 are compared with those in U-23Zr/Fe-Cr, U-23Zr/Fe and U/Fe-Cr. Total diffusion layer thickness growth rate in U-33Mo/T91was one order lower than that in U-23Zr/Fe, at 650 °C [6.14]. Even at 700 °C, the total diffusion layer thickness in U-33Mo/T91 (115 μ m in U-33Mo/T91 (Table 6.1) and 580 μ m in U-23Zr/Fe-12Cr) was significantly (~5 times) lower than that in U-23Zr/Fe-12Cr [6.13]. Similarly, at 700 °C, the total interaction-layer growth rate in U-33Mo/T91 (5.4×10⁻¹⁵ m²/sec) was significantly (~2 order) lower than that in U-23Zr/Fe-12Cr (1.41×10⁻¹³ m²/sec). These results further confirm that auto-generated Mo layer had reduced inter-diffusion between slug and clad and thus resulting in reduced fuel-clad chemical interaction.

Diffusion Layers Growth rate Growth rate Growth rate at Pre-Activation at 650°C at 675°C 700°C exponential couple energy (m^2/sec) (m^2/sec) (m^2/sec) factor (ko) (kJ/mol) m²/sec 1.67×10⁻¹⁶ U-33Mo/T91 0.79×10^{-16} 12.75×10⁻¹⁶ 1.60×10^{7} 406 Clad – Wastage, UFe₂ (major phase)+U₆Fe (L1+L2) U_6 Fe (L4) 8.44×10⁻¹⁶ 12.18×10⁻¹⁶ 10.48×10⁻¹⁶ 1.47×10^{-13} 32 9.37×10⁻¹⁶ 15.15×10⁻¹⁶ 15.31×10⁻¹⁶ Slug - 1.55×10^{-11} 74 penetration, Moautogenous+ $U_6Fe(L3+L4)$ 1.53×10⁻¹⁵ 5.40×10⁻¹⁵ Total Thickness 1.54×10^{-15} 2.20×10^{-4} 184 0.53×10^{-16} 7.11×10^{-16} U/Fe-16 UFe₂ NA 322.3 NA at.%Cr [6.8] Clad-Wastage 21.02×10^{-15} 38.66×10⁻¹⁶ U₆Fe NA NA 219.7 Slug-penetration 48.28×10⁻¹⁶ 2.94×10^{-14} **Total Thickness** NA NA 230.8 0.80×10^{-15} U-23Zr/Fe Clad-wastage 1.10×10^{-15} 1.10×10^{8} 426.4 NA [6.14] $UFe_2 +$ $U_6Fe+ZrFe_2$ 9.17×10⁻¹⁵ 2.85×10⁻¹⁴ NA Slug-penetration NA NA (at 680 °C) 1.30×10^{-14} **Total Thickness** 3.30×10⁻¹⁴ NA 296.6 6.50×10^2 (at 680 °C) Total Thickness U-23Zr/Fe-NA NA 2.28×10^{-10} NA NA 12at.%Cr [6.13] 0.31×10^{-16} α-U-NA NA NA 414 UFe₂ Fe(single crystal)[6.25] 3.11×10⁻¹⁶ U₆Fe NA NA NA 309 7.63×10⁻¹⁶ 15.21×10^{-16} UFe₂ NA NA 234 α/β -U-Fe (poly crystal) (average) [6.8] 59.44×10⁻¹⁶ 117.97×10^{-16} U₆Fe NA NA 127 (average)

Table 6.5 . The growth constant (m^2 /sec) calculated at three different temperatures for UFe₂ and U₆Fe layers for calculation of activation energy

Diffusion couple	Temperature(°C)	Total	Rate
Fuel(at%) /Clad	/time (day)	thickness	constant of
		(µm)	total layer
			growth
			(m ² /sec
U-33Mo/T91	650/14,30,85	63,102,154	1.53*10 ⁻¹⁵
	675/7,14,40	62,85,138	1.535*10 ⁻¹⁵
	700/3,7,15	38,85,115	$5.4*10^{-15}$
U-23Mo/	750/0.21	100	$5.4*10^{-12}$
Fe-13Cr [6.12]			
U-23Zr/Fe-12 Cr	650/14	200	Not enough data
[6.13]	700/4,14	280,580	$1.41*10^{-13}$
	715/1.67	250	Not enough data
U-22.5Zr/Fe	630/4	52.95	4.1*10 ⁻¹⁵
[6.14]	650/4	94.17	1.3*10 ⁻¹⁴
	680/4	151.68	3.3*10 ⁻¹⁴
U-23Zr/Fe	650/10.67,16.95,	100,160,225	9*10 ⁻¹⁵
[6.13]	34.66		
	700/1.67,4,14	115,140,310	$4.12*10^{-14}$

Table 6.6: The total interaction layer growth of different diffusion couples



Fig. 6.11 The comparison of total growth rate between U-33Mo/T91 and other authors. It clearly showing U-33Mo/T91 has much lower growth rate than other diffusion couples.

6.3 Summary

The inter-diffusion microstructure of U-33 at.% Mo - T91 diffusion couples consists of four layers, L1 (U(Fe,Cr)₂+ θ + τ), L2 (U₆Fe), L3 (Mo-autogenous layer) and L4 (U₆Fe+(Mo) lamellar layer). The L1 and L2 layers were present in clad-wastage zone. The slug-penetration zone consists of L3, L4 layers.

> The growth of multi-layer follows parabolic law and the parabolic growth constants were evaluated at three different temperatures.

In U-33Mo/T91 diffusion couple, autogenous-Mo layer acts as a diffusion barrier which reduces clad-wastage. The slower diffusion of Fe through this layer also ensures thinner slug-penetration zone compare to U/Fe-16 at.%Cr, α/β -U-Fe, U-23Zr/Fe and U-23Zr/Fe-12at.%Cr diffusion couple.

The diffusion couple results were superimposed on equilibrium U-Mo-Fe ternary phase diagram at 700°C to understand the diffusion path of the elements.

The parabolic growth constant (K_p) for clad-wastage (L1+L2), U₆Fe (L4) and slug penetration zone (L3+L4) were calculated. The growth rate of slug penetration zone is significantly less in U-33 at.% Mo/T91 diffusion couple compared to diffusion couple of pure U/Fe-16 at.% Cr. However, the growth rate of clad-wastage zone is almost comparable with that of U/Fe (single crystal), U/Fe-16at.%Cr and α/β -U-Fe but lower than that in U-23Zr/Fe couple.

The total interaction layer growth rate in U-33Mo/T91 is significantly lower than in U-23Zr/Fe-12 at.%Cr, U-23Zr/Fe and U/Fe-Cr. This indicates that the formation of Mo-rich layer due to extra Mo content in U-33 at.% Mo alloy acts as a diffusion barrier for U as well as Fe, thus generating thinner interaction zone.

These experiments show that during interaction of U-Mo fuel with Fe-based clad, a protective layer is generated in-situ. A similar protective rind in the form of ZrN layer is possibly formed during fabrication of U-Zr fuel.

6.4 References

6.1. R.G. Pahl, D.L. Porter, D.C. Crawford, L.C. Walters, J. Nucl. Mater., 188 (1992) 3-9.
doi:10.1016/0022-3115\(92\)90447-S.

6.2 W.J. Carmack, H.M. Chichester, D.L. Porter, D.W. Wootan, J. Nucl. Mater., 473
(2016) 167-177. doi:10.1016/J.JNUCMAT.2016.02.019.

6.3. S. Bremier, K. Inagaki, L. Capriotti, P. Poeml, T. Ogata, H. Ohta, V.V. Rondinella, J. Nuc. Mater., 480 (2016) 109-119.

6.4 J. M. Harp, D. L. Porter, B. D. Miller, T. L. Trowbridge, W. J. Carmack, J. Nucl. Mater. 494 (2017), 227-239.

6.5 W. J. Carmack, Temperature and Burnup Correlated FCCI in U-10Zr Metallic Fuel, INL/EXT-12-25550H, (2012) 5-23.

6.6 A. Karahan, J. Buongiorno, M. Kajimi, Modelling of Metallic Fuel for Liquid Metal Fast Reactors, Annual Progress Report (FY2007), 2008.

6.7 J. Ryu, B. O. Lee, S. J. Oh, J. H. Kim, C. B. Lee, J. Nuc. Mat. 392 (2009) 206-212.

6.8 Ke Huang, Diffusion and reaction in selected uranium alloy systems, thesis at University of Central Florida, Orlando, Florida (2012), http://stars.library.ucf.edu/cgi/viewcontent.cgi?article=3391&context=etd.

6.9 D.D. Keiser, Jr., M.A. Dayananda, Metal. Mat. Trans. A , 25A (1994) 1649-1653.

6.10 C. T. Lee, H. Kim, T. K. Kim, C. B. Lee, J. Nuc. Mater. 395 (2009) 140–144.

6.11 A. Aitkaliyeva, J. W. Madden, B. D. Miller, C. A. Papesch, J. I. Cole, J. Nucl. Mater.464 (2015) 28–35.

6.12 S. N. Nikitin, D. P. Shornikov, B. A. Tarasov, V. G. Baranov, Mater. Sci. Engg 130
(2016) 012023, doi:10.1088/1757-899X/130/1/012023.

6.13 K. Nakamura, T. Ogata, M. Kurata, A. Itoh, M. Akabori, Journal of Nuclear Materials275 (1999) 246-254.

6.14 Y. Park, K. Huang, A. Paz Y Puente, H.S. Lee, B.H. Sencer, J.R. Kennedy, Y.H. Sohn, Metal. Mat. Trans. A, 46A, (2015), 72-82.

6.15 Armando Fernández Guillermet, Bull. allo. pha. diag., 3(3)1982, 359-367, doi: 10.1007/BF02869315.

6.16 L.V. Pavlinov, A.I. Nakonechnikov, V.N. Bykov, Translated from Atomnaya Energiya, 19(6)(1965) 521-523.

6.17 S. J Rothman: Diffusion In Uranium, its Alloys and Compounds, 1961, ANL-5700, part C, Metals, Ceramics and Materials (TID-4500, 16th Ed.) AEC Research and Development Report.

6.18 Y.Adda, A. Kirianenko, J. Nuc. Mater., 6(1) (1962) 135-136.

6.19 N. L. Peterson and S. J. Rothman, Phys. Rev., 136(3A) (1964) A842-A849.

6.20 Kiyohiko Nohara, Ken-ichiHirano, Journal of the Japan Institute of Metals 37(7), July1973, 731-736, doi: 10.2320/jinstmet1952.37.7_731,

www.jstage.jst.go.jp/article/jinstmet1952/37/7/37_7_731/_pdf/-char/en.

6.21 T. Chen, T. A. Smith, J. G. Gigax, D. Chen, R. Balerio, L. Shao, B. H. Sencer, J. R. Kennedy, J. Nuc. Mater., 467 (2015) 82-88.

6.22 X. Zhang, Y.F. Cui, G.L. Xu, W.J. Zhu, H.S. Liu, B.Y. Yin, Z.P. Jin, J. Nuc. Mate.
402 (2010) 15–24, doi:10.1088/1757-899X/9/1/012023.

6.23 V.B. Rajkumar, K.C. Hari Kumar, J. Alloys. Comp. 611 (2014) 303–312.

6.24 M. Kurata, IOP Conf. Ser.: Mater. Sci. Eng. 9 (2010),012023.

6.25 T. Chen, T. A. Smith, J. G. Gigax, D. Chen, R. Balerio, L. Shao, B. H. Sencer, J. R. Kennedy, J. Nuc. Mater. 467 (2015) 82-88.

Chapter 7: Conclusions & Scope For Further Research

7.1. Conclusions

U-Mo fuel is presently used as monolithic fuel for research reactor application with Al base alloys as a clad material. Wheras, U-Zr/U-Pu-Zr alloy is selected as fast reactor metallic fuel. Present study aims investigation of U-Mo alloy for fast reactor applications, as it has following advantages.

- > 'Mo' addition in 'U' stabilizes isotropic γ -(U) phase (bcc)
- γ Phase stability of U-Mo fuel is over a wider temperature range, therefore it is more suitable for reactor operations than U-Zr fuel. As the cubic γ-(U) phase is isotropic, it provides advantage of isotropic expansion and uniform thermo-physical property, like thermal conductivity. The cubic γ phase also has advantage of higher solubility of alloying elements and fission product elements, which minimizes fuel constituent migration and fission product redistribution during reactor operation
- > With Mo, hardness increases and it is also has higher thermal conductivity.

The metallic fuels are normally prepared by injection casting. However, in the reactor these fuel microstructure tends to attain equilibrium structures due to higher temperature and longer in-reactor stay. Therefore, it is important to understand the microstructure of U-Mo alloys formed in as-cast and possible microstructural changes during reactor operation. Hence, four different U-Mo alloys (2, 5, 10 and 33 at.% Mo) were made. Microstructure, XRD and micro-hardness of as-cast and annealed alloys were compared. Microstructure were characterized using optical microscope, SEM along with EDS and EBSD analysis, XRD and micro-hardness measurement. Reitveld analysis was also performed for in-depth analysis of XRD pattern and determination of lattice parameter of the U-Mo alloys. Additionally, phase field

model was developed for mechanistic understanding of solidification/cast microstructure for U-33 at.% Mo system using entropy functional and experimentally determined diffusivity data reported in the literature. This model provides basic understanding of the effect of different kinetics and thermodynamic parameters on solidification and micro- segregation behaviour of the alloy during casting of U-Mo alloys.

Fuel clad chemical interaction between U-33 at.% Mo fuel vs T91 clad was investigated to understand the inter-diffusion of different elements of U-Mo slug and T91 clad. The diffusion path of the system was analysed with ternary equilibrium phase diagram. The interaction zone microstructure between U-33Mo and T91 was analysed with SEM-EDS.

Following are the important outcome of the study:

(a) Microstructural analysis of as-cast and annealed u-Mo alloys.

(i) U-2 at.% Mo and U-5 at.% Mo have orthorhombic α -phase in as-cast condition. The Rietveld analysis of as-cast alloys indicated insignificants variation of lattice parameter with the change in Mo content.

(ii) As-cast U-10 at.% Mo alloy had monoclinic α'' phase and XRD pattern showed splitting of (131) line into ($\overline{1}31$) and (131) of unequal intensities confirming the presence of monoclinic phase. This was confirmed by Rietveld analysis revealed three split lines viz. (111), (112) or (131).

(iii) The annealed U-2 at.% Mo and U-5 at.% Mo alloys had orthorhombic α -U phase. Whereas, annealed U-10 at.% Mo had orthorhombic α -(U) phase and tetragonal U₂Mo phase. The Rietveld method quantifies the volume percent of α -U and U₂Mo as 77.8 % and 22.2 %, respectively. Whereas, annealed U - 33 at.% Mo has ordered U₂Mo intermetallic phase. (iv) As-cast 33 at.% Mo alloy had cubic γ -(U) phase with dendritic microstructure having secondary branching. The microstructure also showed the presence of a small fraction of equiaxed bcc-(Mo) dendrites. The Rietveld plot showed good fit with cubic γ -U structure, with slight shrinkage in lattice parameter: 0.353 nm for pure γ -U and 0.338 nm for γ -(U) for as-cast alloy with 33 at.% Mo. EBSD analysis indicated no preferred orientation of as-cast dendrites in U-33 at.%Mo alloy.

(b) More detailed investigations were carried out with U-33 at.% Mo as this represents an alloy with maximum Mo content that has γ -(U) phase in ambient temperature to ~ 1284°C. This alloy has maximum Mo that doesn't have Mo phase at low temperatures, in equilibrium condition. SEM-EDS analysis showed considerable degree of micro-segregation in both types of dendrites. The evolution of morphology and micro-segregation of γ -(U) and (Mo) dendrite from the melt of U-33 at. % Mo have been simulated with WBM model based on phase field concept. Adaptive unstructured mesh was used for the simulation. The important findings of the phase field modelling are listed below:

(i) The detailed SEM-EDS analysis of equiaxed (Mo) dendrite showed midrib concentration 90-94 at.% and peripheral concentration is 83-87 at.%. The PFM simulation of (Mo)-dendrite shows similar concentration distribution assuming nearly equal U and Mo diffusivity in solid and liquid phase. The diffusivity in liquid phase was assumed to be one order higher than solid diffusivity. The tip velocity was found to be in the range of 0.3-0.4 m/sec and it increased with increasing undercooling. The tip temperature of dendrite were found to rise during evolution process.

(ii) The microsegregation in γ -(U) dendrite was also simulated at different undercoolings. The simulated concentration profile matched very closely with experimental values. The simulation showed increasing tip velocity with increasing undercooling. It was

found that the tip temperature increased monotonically during growth of primary dendrites. After generation of secondary branch the tip temperature vary non-monotonically with time.

(c) Hardness of annealed alloys was found to increase with increase in 'Mo' content due to presence of two phase microstructure. Annealed single phase U-33 at.% Mo alloy shows slight reduction in hardness than biphasic α -U+U₂Mo.

(d) The inter-diffusion microstructure of U-33 at.% Mo vs. T91 diffusion couples consists of four layers, L1 (U(Fe,Cr)₂+ θ + τ), L2 (U₆Fe), L3 (Mo-autogenous layer) and L4 (U₆Fe+(Mo) lamellar layer). The growth of multi-layer follows parabolic law and the parabolic growth constants were evaluated at three different temperatures. The following are some of the important conclusion arrived from those analysis

(i) The inter-diffusion zone microstructure can be divided into two zones, (i) clad-wastage zone and (ii) slug-penetration zone. The L1 and L2 layers were observed in clad-wastage zone. The slug-penetration zone consists of L3, L4 layers.

(ii) In U-33Mo/T91 diffusion couple, autogenous-Mo layer acts as a diffusion barrier which reduces clad-wastage. The slower diffusion of Fe through this layer also ensures thinner slug-penetration zone compare to U/Fe-16 at.%Cr, α/β -U-Fe, U-23Zr/Fe and U-23Zr/Fe-12at.%Cr diffusion couple.

(iii) The calculated U-Mo-Fe ternary diagram shows equilibrium phase regions. However, due to formation of Mo layer, inter-diffusion zone of U-33Mo/T91 diffusion couple did not reach equilibrium. Hence, two phase lamellar region comprising of U_6Fe and Mo-bcc phase formed in the slug.

(iv) The parabolic growth constant (K_p) for clad-wastage (L1+L2), U₆Fe (L4) and slug penetration zone (L3+L4) have been calculated. The growth rate of U₆Fe lamellar layer is significantly less in U-33 at.% Mo/T91 diffusion couple compared to diffusion couple of

pure U/Fe-16 at.% Cr. Similarly, the growth rate of both, clad-wastage and slug penetration zone is significantly less in U-33 at.% Mo/T91 compared with U-23Zr/Fe and α/β -U-Fe.The total interaction layer growth rate in U-33Mo/T91 is significantly lower than in U-23Zr/Fe-12 at.%Cr, U-23Zr/Fe and U/Fe-Cr. This indicates that the formation of Morich layer (higher Mo content in the fuel) acts as a diffusion barrier for U as well as Fe, thus generating thinner interaction zone.

7.2. Scope For Further Research

The present study opens up many important directions for further research in the field of development of U-Mo alloys for nuclear applications. Some of the important issues are as listed below:

1. Calculation of breeding ratio of U-Mo fuels with different Mo composition in fast reactor spectrum.

2. Fuel clad interaction study with oxide dispersed steel will provide important insight on the feasibility using ODS as clad in U-Mo fuel.

3. Parametric study involving anisotropy, temperature gradient and their effect on secondary arm spacing or primary phase morphology will provide more insight into dendritic crystal growth. Development of phase field model to predict peritectic phase transformation in U-Mo alloy.

4. The creep and fatigue data will be generated for these alloys and as well as irradiation performance of the alloy will be carried out.

5. Further studies need to be carried out to optimize molybdenum content of the fuel, to get the Mo-autogenous barrier layer and desired solidus temperature while achieving required fissile atom density.

6. Further in-pile studies are required to assess the effectiveness of Mo-autogenous layer in the reactor operating conditions to understand the effect of fission-products and temperature gradient.

Appendix 1

PDF-code of the phases present in U-Mo fuel and clad T91:

Phase	Crystal	Space	Formul	Lattice parameter(nm)			PDF Card No.
	System	group(Space	а	а	b	с	
		Group no)					
α-U	orthorhomic	Cmcm(63)	U	0.285	0.585	0.495	00-011-0628
α"-U	monoclinic	C2/m(12)	U	0.283	0.489	0.3308	00-001-1195
γ-U	cubic	lm 3 m(229)	U	0.347	0.347	0.347	00-024-0749
γ'-U ₂ Mo	tetragonal	I4/mmm(13	U2Mo	0.343	0.343	0.983	01-071-9825
		9)					
UO ₂	cubic	Fm 3 m(225)	UO2	0.547	0.547	0.547	01-071-4823
UFe ₂	cubic	Fd-3m(227)	UFe ₂	0.7061	0.7061	0.7061	00-018-0661
U ₆ Fe	tetragonal	I4/mm(140)	U ₆ Fe	1.0272	1.0272	0.52436	01-071-8442
				4	4		
Bcc	cubic	lm-3m(229)	Мо	0.1147	0.1147	0.11474	01-071-3771
(Mo)				4	4		
Bcc (Fe)	cubic	lm-3m(229)	Fe	0.2866	0.2866	0.28665	01-071-3763
				5	5		