

---

# INVESTIGATION OF HIGH-ENTROPY ALLOYS FOR USE IN ADVANCED NUCLEAR APPLICATIONS

---

*A thesis submitted in partial fulfilment for the degree of doctor of philosophy at University of Technology  
Sydney*

Daniel J. M. King

## Certificate of Authorship / Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis

Signed:

## Acknowledgements

The occurrence and fruition of this project was one born from serendipity, ultimately beginning with my dear wife, Shirin-Rose King. Her role in the completion of this PhD, through both emotional and practical support, has been constant over the past three years and I am very thankful. It was through her that I was able to attend a week-long visit to ANSTO where I met Dr. Simon Middleburgh who proposed the current project. I may never meet another person such as Simon. There are very few people who can consistently induce confidence in oneself and abilities. A natural leader, his passion, curiosity and work ethic is incredibly inspiring and I attribute a lot of the success of this PhD to his unwavering guidance, support and boundless knowledge. I remember the first day I started my PhD, two students from Imperial College London (now Dr. Hassan Tahini and Dr. Patrick Burr) were visiting ANSTO. We all huddled around Simon's desk in excitement over a new finding like children who had found a strange insect. It was then that I knew that that research was the right path for me.

Of course, none of this would have been possible without Prof. Michael Cortie who supported this project after overhearing me lamenting over the fact I could not find an academic that was willing. Although lecturing is not his favourite past time, he was my favourite teacher during undergraduate studies due to his casual yet concise teaching style. Over the past three years it seems he would consign an infinite amount of time to assist in any problem I had, despite having such a busy schedule. Patient, wise and empathetic, one could not ask for a better mentor.

There are many others that have been of great help to the completion of this project. Namely: Dr. Amelia Liu, a collaborator who treated me like family when I visited Monash University while writing my very first, first name publication, Dr. Daniel Riley who provided insightful technical and practical knowledge as well as a shoulder to lean on, Dr. Timothy Lucey, Dr. Gordon, Dr. Greg Lumpkin, Dr. Edward Obbard, Dr. Patrick Burr, Dr. Massey De Los Reyes, Technicians: Ken Short, Tim Palmer, Kim Lu, Angus Gentle and Geoff McCredie whose contributions were invaluable. Last but not least, I must thank my second cousin, Andrew McGregor, who selflessly dedicated a large amount of his spare time to build the ASAP software and web-integration, tying together a large portion of my work.

## Abstract

A preliminary assessment of the suitability of high-entropy alloys (HEAs) for use within a nuclear reactor environment is conducted by combining both experimental and computational techniques. The investigation begins on the V-Zr system where three thin films with stoichiometries (2V:1Zr, 1V:1Zr and 1V:2Zr) were deposited. A metastable amorphous phase was observed and subsequently modelled, for the first time, using static density functional theory (DFT). This methodology is then further developed and the thermodynamics of the binary system were assessed.

Similar computational techniques were then used to investigate CoCrFeNi. Isolated vacancy formation calculations were performed and it was found that vacancies of Co, Fe and Ni are positive, and Cr is negative in energy. This drive for spontaneous segregation of Cr from the FCC matrix is predicted to occur in a vacancy mediated process. It is possible that this mechanism will allow for the formation of a corrosion resistant oxide layer. The addition of Al to form the  $\text{Al}_x\text{CoCrFeNi}$  system, where  $x$  is varied from 0 – 2.4 atomic ratio, was then explored. Only when partial ordering was imposed, with Al and Ni restricted to separate sub-lattices, to form an ordering analogous to the B2 NiAl intermetallic, was the BCC packing stable. Decomposition of the ordered BCC single phase into a dual phase (Al-Ni rich and Fe-Cr rich) was also considered.

An algorithm to rapidly screen elemental mixtures to form single phase high-entropy alloys (SPHEAs) was developed. Approximately 186,000,000 compositions of equimolar 4, 5 and 6 element alloys were screened and ~1900 new SPHEAs were predicted using this method.

$\text{NbTiV}$ ,  $\text{Mo}_{0.5}\text{NbTiV}$ ,  $\text{MoNbTiV}$ ,  $\text{NbTiVZr}_{0.5}$ ,  $\text{NbTiVZr}$  and  $\text{NbTiVZr}_2$  were experimentally produced via arc melting. As predicted by the screening method, all alloys were found to form a single phase BCC structure with non-equilibrium dendritic microstructures.  $\text{Au}^{5+}$  and  $\text{He}^+$  ions were used to irradiate TEM samples and a bulk  $\text{NbTiVZr}_2$  sample. No changes were observed after ~20-25 dpa in the TEM samples and minimal swelling of the BCC matrix was observed in the bulk sample.

The project has revealed that HEA alloys are potentially candidate materials for structural applications in nuclear reactor environments.

# Contents

Certificate of Authorship / Originality .....	i
Acknowledgements .....	ii
Abstract .....	iii
1 LITERATURE REVIEW.....	9
1.1 Introduction .....	10
1.2 The nuclear industry .....	11
1.3 Previous and current nuclear materials.....	13
1.3.1 Zirconium alloys .....	13
1.3.2 Iron alloys .....	13
1.3.3 Nickel-based alloys .....	14
1.4 High-entropy alloys .....	14
1.4.1 Morphology and microstructure.....	18
1.4.2 Mechanical Properties .....	23
1.4.3 Oxidation and Corrosion .....	24
1.4.4 Simulation of HEAs .....	26
2 METHODOLOGY .....	29
2.1 Density functional theory .....	30
2.1.1 Born-Oppenheimer approximation .....	31
2.1.2 Electron density functional .....	31
2.1.3 Exchange-correlation .....	32
2.1.4 Periodic boundary conditions.....	33
2.1.5 Pseudopotentials.....	37
2.2 Modelling disordered systems .....	37
2.3 Defect energies .....	39
2.4 Miedema's model .....	39
2.4.1 Intermetallic compounds .....	41
2.4.2 Concentrated solid solutions .....	42
2.4.3 Amorphous alloys .....	43
2.4.4 Application to HEAs .....	44
2.5 Magnetron sputtering.....	44
2.6 Vacuum arc melting .....	45

2.7	Metallurgical surface preparation .....	46
2.8	X-ray diffraction .....	47
2.9	Simulated XRD patterns .....	48
2.10	Scanning electron microscopy .....	49
2.11	Transmission electron microscopy .....	50
2.12	Ion irradiation .....	51
2.12.1	SRIM .....	52
2.13	Neutron cross-section .....	53
2.14	Nanoindentation .....	54
3	FORMATION AND STRUCTURE OF V-Zr AMORPHOUS ALLOY THIN FILMS .....	55
3.1	Introduction .....	56
3.2	V-Zr thin films .....	57
3.3	Modelling the amorphous structures .....	58
3.4	Thermodynamic stability of the phases .....	63
3.4.1	V <sub>2</sub> Zr .....	64
3.5	In the context of HEAs .....	65
3.6	Summary .....	66
4	AB INITIO INVESTIGATION OF THE Al <sub>x</sub> CoCrFeNi HIGH-ENTROPY ALLOY .....	67
4.1	Introduction .....	68
4.2	CoCrFeNi .....	68
4.3	Al <sub>x</sub> CoCrFeNi .....	72
4.4	Phase Stability .....	75
4.4.1	Phase segregation .....	76
4.5	Summary .....	77
5	PREDICTING THE FORMATION AND STABILITY OF SINGLE PHASE HIGH-ENTROPY ALLOYS .....	79
5.1	Introduction .....	80
5.2	Previous methods .....	81
5.3	The $\Phi$ value .....	84
5.3.1	Assessing the accuracy .....	84
5.3.2	Benchmarking to experimental literature .....	87
5.4	Predicting precipitation temperatures .....	89
5.5	Exploring the Co-Cr-Fe-Ni system .....	90
5.6	Exceptions to the model .....	91
5.7	Predicting new high-entropy alloy systems .....	92

5.8	Summary .....	95
6	RADIATION DAMAGE IN Nb-Ti-V-Zr AND Mo-Nb-Ti-V HIGH-ENTROPY ALLOYS .....	96
6.1.	Introduction .....	97
6.2	As-cast alloys .....	98
6.2.1	NbTiV .....	99
6.2.2	Mo <sub>0.5</sub> HEA and MoHEA .....	100
6.2.3	Zr <sub>0.5</sub> HEA and ZrHEA.....	103
6.2.4	Zr <sub>2</sub> HEA .....	106
6.3	Predicted performance.....	106
6.3.1	Mechanical performance.....	106
6.3.2	Neutron cross sections.....	107
6.3.3	Stability .....	108
6.3.4	Radiation tolerance.....	109
6.3.4.1	Vacancy defects .....	110
6.3.4.2	Interstitial defects .....	111
6.3.4.3	Frenkel defects .....	112
6.3.4.4	Ion irradiation.....	114
6.3.4.4.2	Zr <sub>2</sub> HEA bulk sample .....	120
6.4	Summary .....	123
7	CONCLUSIONS AND FUTURE WORK.....	125
	References.....	129
	Appendix.....	141

# List of Figures

Figure 1.1. Number of publications on the topic “high-entropy alloys” as searched in Web of Science. ....	11
Figure 1.2. Taken from Yang <i>et al.</i> 2012 [43], where $\Omega$ and $\delta$ are plotted for an experimentally characterised system that has been determined to form a single phase solid solution (black squares), dual phase solid solution + intermetallic (blue triangles), intermetallics (red circles) and BMGs (cyan triangles).....	17
Figure 1.3. Taken from Yeh <i>et al.</i> 2004 [5], shows: A. Hardness, B. FCC and C. BCC lattice constants of the $\text{Al}_x\text{CoCrCuFeNi}$ HEA when $x$ (in atomic ratio) is increased from $0 \rightarrow 3$ .....	19
Figure 1.4. Taken from Wang <i>et al.</i> 2012 [57] showing optical micrographs of the as-cast samples displaying a columnar cellular structure (a – c), columnar dendrite (d – f), equiaxed nondendritic grain (g – h), equiaxed dendritic grain (i – l), and a non-equiaxed dendritic grain structure (m – n). ....	20
Figure 1.5. BSE image of (a) drop-cast $\text{CoCrFeNi}$ and (b) crucible quenched $\text{CoCrFeMnNi}$ taken from Wu <i>et al.</i> 2014 [66] and Salishchev <i>et al.</i> 2014 [73], respectively. ....	22
Figure 1.6. SEM micrographs from Senkov <i>et al.</i> 2014 [78] of (a) equiaxed grain structure and (b) sub-grain structure of $\text{Al}_{0.4}\text{Hf}_{0.6}\text{NbTaTiZr}$ after annealing at 1473 K for 24 hrs. ....	23
Figure 1.7. Taken from Zhang <i>et al.</i> 2012 [105] CALPHAD generated pseudo-binary phase diagram through the $\text{Al}_x\text{CoCrFeNi}$ system with varying Al atomic ratio $x$ . ....	26
Figure 2.1. Demonstration of convergence of k-points for elements (grouped by HEA system), studied within this dissertation. ....	34
Figure 2.2. Convergence of the plane-wave cutoff energy ( $E_{\text{cut}}$ ). The black dashed line represents the $E_{\text{cut}}$ values used when performing calculations on the elements plotted. ....	36
Figure 2.3. The effect of incremental increase in BCC supercell size from $2 \times 2 \times 2$ (16 atoms), $3 \times 3 \times 3$ (54 atoms) and $4 \times 4 \times 4$ (128 atoms) on free energy using the brute force method with the average energies (black crosses) plotted within the spread of energies (error bars). Compared to the SQS method (blue crosses) and the average CPU times on the secondary y-axis (red crosses). ....	38
Figure 2.4. Taken from Bakker [145], $ \Delta\phi $ vs $ \Delta n_{WS}^{1/3} $ for solid binary alloys of transitional metals where a solid circle represents compound formation and a cross represents either no intermetallic or both solid solubilities are smaller than 10 at. %. Noticeable discrepancies above the line are Cr-Fe, Cr-U, Cu-Rh and Hf-U; below the line – Au-Cr, Ca-Pr, Cr-Mn, Cr-Mo and Cu-Mn. ....	40
Figure 2.5. Taken from Bakker [145], a two dimensional representation of the surface contact between unlike atoms in an ordered system using the macroscopic atom model. ....	41
Figure 2.6. Diagram of magnetron sputtering chamber setup with vacuum pumps and sample load locking mechanism. ....	45
Figure 2.7. Top view and side view of arc melted button with sections in red. ....	46
Figure 2.8. Standard Bragg-Brentano experimental XRD setup with GIXRD tube angle of incidence $\omega$ denoted by the red arc. ....	48
Figure 2.9. Taken from Ref. [164] typical neutron cross-section vs neutron energy relationship. ....	54
Figure 3.1. Glass-forming zone in the V–Zr system (adapted and redrawn from Eickert <i>et al.</i> [170]). ....	56
Figure 3.2. Experimental XRD patterns (dashed) for 1V:2Zr (red), 1V:1Zr (black) and 2V:1Zr (blue) amorphous thin films with the CPL indicated by vertical solid lines of matching colour. Representative (b) selected-area diffraction pattern of the 1V:1Zr film and (c) BF-STEM image of	

the same amorphous film demonstrating its amorphous nature (taken by Dr. Amelia Liu, Monash University, Australia).....	58
Figure 3.3. Average simulated XRD patterns of optimised (A) 1V:2Zr, (B) 1V:1Zr and (C) 2V:1Zr supercells with starting edge lengths of 11 Å, 10 Å and 9 Å located at the top, middle and bottom, respectively. These patterns are compared to (D) (1V:1Zr) <sub>BCC</sub> (grey) and V <sub>2</sub> Zr (black) simulated XRD patterns.....	59
Figure 3.4. Lattice energy per atom (normalized to V <sub>2</sub> Zr) vs. volume per atom of amorphous supercells of 1V:2Zr (top), 1V:1Zr (middle), 2V:1Zr (bottom) with starting densities of 9 Å (a) converged to 10 <sup>-3</sup> eV (blue square), (b) converged to 10 <sup>-4</sup> eV (magenta diamond), 10 Å (red circle) and 11 Å (green triangle) with V <sub>2</sub> Zr as reference (cross). ....	60
Figure 3.5. Average simulated XRD patterns (dashed) for 11 Å 1V:2Zr (red), 1V:1Zr (black) and 2V:1Zr (blue) amorphous supercells with the central peak location (CPL) indicated by vertical solid lines of matching colour.....	61
Figure 3.6. Average simulated radial distribution functions (dashed) for 2V:1Zr (red), 1V:1Zr (black) and 1V:2Zr (blue) amorphous supercells with the CPL of the first, second and third nearest neighbours indicated by vertical solid lines of matching colour.....	62
Figure 3.7. Calculated average interatomic distances to the first nearest neighbour for 1V:2Zr, 1V:1Zr and 2V:1Zr (crosses), compared to the modelled ideal crystalline structures of BCC V (circle), HCP Zr (diamond) and BCC Zr (square) and V <sub>2</sub> Zr (triangle). Two linear functions (red and blue), representing Vegard's law, are fitted between bcc V and HCP Zr, and BCC V and BCC Zr, respectively. ....	63
Figure 4.1. Vacancy formation energy for Co, Cr, Fe and Ni in CoCrFeNi HEA as a function of supercell stability. The average value is highlighted with a dashed line for each species. ....	69
Figure 4.2. Vacancy formation energy for Cr, Co, Fe and Ni in Cr <sub>0.55</sub> CoFeNi HEA as a function of supercell stability. The average value is highlighted with a dashed line for each species. ....	69
Figure 4.3. Defect energy of interstitial species in CrCoFeNi as a function of lattice stability. Mean defect energies are highlighted as a dashed line for each species. ....	70
Figure 4.4. Partially ordered structures with BCC packing include: (i) Al and Ni constrained to the centre and corner sites, respectively, and (ii) Al constrained to the centre site. (iii) Is the partially ordered L1 <sub>2</sub> structure with Fe constrained to the FC-site. In these models Al is represented as red, Ni – green, Fe – gold, Co – light blue, Cr – dark blue. ....	72
Figure 4.5. Simulated XRD patterns of FCC Al <sub>x</sub> CoCrFeNi with $x = 0.00, 0.57, 1.33$ and $2.40$ . The peaks are indexed as follows: (a) (111), (b) (200), (c) (220), (d) (311), and (e) (222).....	73
Figure 4.6. Simulated XRD patterns of BCC Al <sub>x</sub> CoCrFeNi with $x = 0.91, 1.40$ , and $2.00$ . Peaks labelled with the • symbol are the ideal BCC peaks [from low to high angle these are indexed as (110), (200), (211), and (200)], while the * indicates the (100) ordering peak.....	74
Figure 4.7. Simulated XRD pattern of BCC Al <sub>2</sub> CoCrFeNi with simultaneous ordering of Al and Ni on separate sublattices. The * symbols highlight the experimentally observed ordering peaks [57].	74
Figure 4.8. Calculated variation in Gibbs free energy of the disordered and partially ordered (Fe-ordered) CoCrFeNi systems with temperature.....	75
Figure 4.9. Variation in formation enthalpy of Al <sub>x</sub> CoCrFeNi. Completely disordered face-centred cubic (red), Al-ordered body-centred cubic (light blue), and Ni-Al-ordered body centred cubic (blue) structures are plotted. The values for completely disordered body-centred cubic are not included as the simulation predicted this phase to be unstable at all Al contents. ....	76

Figure 5.1. A comparison of 185 systems, experimentally determined to create a solid solution (blue diamond) or intermetallic/multiphase (red circle) structure, plotted for Yang <i>et al.</i> 's predictive parameters whereby $\Omega \geq 1.1$ and $\delta \leq 6.6$ predict the formation of a SPHEA. ....	82
Figure 5.2. A comparison of 185 systems experimentally determined to create a disordered (blue diamond) or ordered (red circle) plotted for: A. Singh <i>et al.</i> 's predictive parameter whereby $\Lambda \geq 0.96$ predict the formation of a HEA and B. Wang <i>et al.</i> 's predictive parameter whereby a value of $\gamma < 1.175$ predicts HEA formation. ....	83
Figure 5.3. Formation enthalpies obtained for various compounds of the Pt-Al system, using: Literature values [212] obtained experimentally (green square) and theoretically (red circle) compared to values obtained from calculations in the current study using DFT (blue triangle) and Miedema's model (magenta diamond).....	85
Figure 5.4. Formation enthalpies for the formation of a BCC solid solution in the Mo-Nb-Ti-V0.25 system comparing values obtained from A. DFT calculations to B. Miedema's model. The colours ranging from green $\rightarrow$ blue denote the formation enthalpies from 4.59 $\rightarrow$ -9.40 kJ/mol. ....	86
Figure 5.5. A comparison of 185 systems experimentally determined to create a solid solution (blue diamond), intermetallic/multiphase (red circle) structure and those that are an exception (green triangle) to the $\Phi \geq 1$ criteria (dashed line) plotted against a geometrical parameter $\delta$ . ....	88
Figure 5.6. A comparison of 185 systems experimentally determined to create a solid solution (blue diamond), intermetallic/multiphase (red circle) and those that are an exception to the $\Phi \geq 1$ criteria (green triangle) plotted against the largest binary enthalpy contribution, $\Delta H_{max}$ . ....	89
Figure 5.7. All possible compositions in the $\text{Co}_a\text{Cr}_b\text{Fe}_c\text{Ni}_d$ system (open coloured circles). Melting temperatures of 1730 $\rightarrow$ 2120 K are represented as colours from blue $\rightarrow$ red. The equimolar CoCrFeNi system (cross) and the segregation of each element Cr (black solid), Co (red solid), Fe (black dashed) and Ni (orange solid) lines are overlayed. The precipitations temperatures at three Cr contents are displayed and $\Phi = 1$ cut-off is denoted by the grey dashed line. ....	90
Figure 6.1. The bulk as-cast NbTiV sample as analysed using (a) SEM backscatter (b) XRD, where the experimental XRD pattern (black line) is compared to the simulated XRD pattern of the DFT model (red line). Reflections of pure Nb and HEA matrix are labelled by the triangles and circles, respectively. ....	100
Figure 6.2. Mo <sub>0.5</sub> HEA (i) experimental XRD pattern (black line) with reflections of pure Mo and HEA matrix labelled by the triangles and circles, respectively. Simulated XRD pattern (red line) of DFT modelled HEA is overlaid for comparison. (ii) SEM-BSE micrographs displaying the contrast in BSE intensity due to the dendrite (lighter) and interdendrite (darker) morphology. ....	101
Figure 6.3. MoHEA (i) experimental XRD pattern (black line) with reflections of pure Mo and HEA matrix labelled by the triangles and circles, respectively. Simulated XRD pattern (red line) of DFT modelled HEA is overlaid for comparison. (ii) SEM-BSE micrographs displaying the contrast in BSE intensity due to the dendrite (lighter) and interdendrite (darker) morphology.....	102
Figure 6.4. SEM-SE image of the polished Zr <sub>0.5</sub> HEA surface where EDS analysis was performed at points 1 – 5 away from the undissolved Nb (light grey on left). Small pores (black regions) are also present. ....	103
Figure 6.5. Zr <sub>0.5</sub> HEA (i) experimental XRD pattern (black line) and simulated XRD pattern (red line) of DFT modelled HEA is overlaid for comparison. (ii) SEM-EDX maps display contrast in colour between regions of Nb (red) and Zr (blue) with Ti (green) and V (yellow) evenly dispersed. ....	104
Figure 6.6. ZrHEA (i) experimental XRD pattern (black line) and simulated XRD pattern (red line) of DFT modelled HEA is overlaid for comparison. (ii) SEM-EDX maps display contrast in colour between regions of Nb (red) and Zr (blue) with Ti (green) and V (yellow) evenly dispersed. ....	105

Figure 6.7. Zr HEA experimental XRD pattern (black line) and simulated XRD pattern (red line) of DFT modelled HEA is overlaid for comparison. Reflections of pure Nb and HEA matrix are labelled by the triangles and circles, respectively.....	106
Figure 6.8. Gibbs free energy at 0 K (blue square) and at the predicted melting temperature (red square) with all temperatures between (solid line) for each system studied within this chapter. Temperatures that intersect $\Delta G = 0$ for the Zr containing HEAs are labelled in Kelvin.....	109
Figure 6.9. SRIM simulated damage profile within the NbTiVZr <sub>2</sub> bulk sample using the default $E_d$ (red dashed), calculated $E_d$ (red solid) and literature $E_d$ (green dashed) using Au <sup>5+</sup> and He <sup>+</sup> (blue) ions.....	115
Figure 6.10. Distribution of Au atoms (red, y <sub>1</sub> -axis) and He atoms (blue, y <sub>2</sub> -axis) as a function of depth in the Zr <sub>2</sub> HEA bulk sample. ....	116
Figure 6.11. (i), (iii) BF-TEM image and corresponding (ii), (iv) SAED pattern of (i), (ii) unirradiated and (iii), (iv) irradiated TEM disks for (a) Mo <sub>0.5</sub> HEA, (b) MoHEA and (c) NbTiV. ..	117
Figure 6.12. (i), (iii) BF-TEM image and corresponding (ii), (iv) SAED pattern of (i), (ii) unirradiated and (iii), (iv) irradiated TEM disks for (a) ZrHEA, (b) Zr <sub>0.5</sub> HEA and (c) Zr <sub>2</sub> HEA.....	118
Figure 6.13. (a) BF-TEM image and (b) corresponding amorphous SAED pattern in the irradiated Zr <sub>2</sub> HEA. ....	119
Figure 6.14. GIXRD patterns of the unirradiated Zr <sub>2</sub> HEA bulk sample with maximum depths in which 99% of the intensity was obtained numerically labelled in $\mu\text{m}$ . Reflections identified as the Nb phase are denoted by the triangle symbol and the ZrHEA matrix as a circle.....	120
Figure 6.15. GIXRD patterns of the post-irradiated Zr <sub>2</sub> HEA bulk sample with maximum depths in which 99% of the intensity was obtained numerically labelled in $\mu\text{m}$ . Reflections identified as the Nb phase are denoted by the triangle symbol. ....	121
Figure 6.16. Comparison between lattice parameters with changing depth within Zr <sub>2</sub> HEA in the as-cast (blue circle), Au <sup>5+</sup> irradiated (red square) and He <sup>+</sup> irradiated (green triangle) state on the y <sub>1</sub> axis. Non-crystalline volume fraction in the Au <sup>5+</sup> irradiated (dashed red line) and He <sup>+</sup> irradiated (dashed green line) state on the y <sub>2</sub> axis.....	122

# List of Tables

Table 1.1. Mechanical property ranges, at room temperature, for conventional alloys where $\rho$ , $E$ , $\sigma_y$ , $\sigma_{uts}$ and $K_{Ic}$ corresponds to density, Young's modulus, yield strength, ultimate tensile strength and fracture toughness, respectively. "Best" values for each property are in bold. ....	24
Table 1.2 Weight gain per area when exposed to oxygen flow at 800 °C for 24 hrs. ....	25
Table 2.1. The range of charge states of Au and their corresponding fraction and final energies. ....	52
Table 3.1. Composition of thin films. ....	57
Table 5.1. 50 predicted equimolar 4 element alloys sorted by price with values (March 2015) of $\Phi$ , $\delta$ , melting temperature ( $T_m$ ) and maximum melting temperature of their elemental constituents ( $T_{max}$ ). ....	92
Table 6.1. Chemical compositions of as-cast alloys provided through EDS analysis using (see Section 2.10). ....	98
Table 6.2. Chemical compositions of 54 atom supercells. ....	99
Table 6.3. Young's modulus and hardness as determined by nanoindentation experiments for the respective systems. ....	107
Table 6.4. Comparison of microscopic thermal neutron absorption cross section ( $\sigma_a$ ), density ( $\rho$ ) (theoretical values in bold) and macroscopic thermal neutron absorption cross section ( $\Sigma_a$ ). ....	108
Table 6.5. Average vacancy formation energies of Mo, Nb, Ti, V, Zr for each respective system compared to the pure BCC metals. ....	110
Table 6.6. Interstitial formation energies in eV (first sub-column) and percentage orientation occurrences (second sub-column) for Mo <sub>0.5</sub> HEA dendrite/interdendrite and MoHEA dendrite/interdendrite and <100>, <110>, <111> and alternate configurations. ....	111
Table 6.7. Interstitial formation energies in eV (first sub-column) and percentage orientation occurrences (second sub-column) for NbTiV, Zr <sub>0.5</sub> HEA, ZrHEA and Zr <sub>2</sub> HEA and <100>, <110>, <111>, AC dumbbell configurations. ....	111
Table 6.8. Average interstitial formation energy of Mo, Nb, Ti, V, Zr for the respective systems compared to the pure BCC metals in a <111> split interstitial orientation (with the exception of Ti and Zr which are HCP basal octahedral). ....	112
Table 6.9. Unbound Frenkel defect energies for each element within each system in eV. ....	113
Table 6.10. Average change in lattice parameters of the HEA supercells with a single vacancy, $v(V_A)$ , and interstitial, $v(A_i)$ defect, with the estimated Frenkel defect 3volume, $v(F_A)$ , in each column, respectively. ....	114
Table 6.11. Average threshold displacement energy of Mo, Nb, Ti and V from their pure BCC metals and theoretically predicted from Frenkel defect energies. ....	115
Table 6.12. Lattice parameter of each sample in the unirradiated and irradiated condition with the difference between the two. ....	119