DFT study of the hexagonal high-entropy alloy fission product system

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Abstract

The metallic phase fission product containing Mo-Pd-Rh-Ru-Tc can be described as a hexagonal high-entropy alloy (HEA) and is thus investigated using atomic scale simulation techniques relevant to HEAs. Contrary to previous assumptions, the removal of Tc from the system to form the Mo-Pd-Rh-Ru analog is predicted to reduce the stability of the solid solution to the point that σ-Mo_5Ru_3 may precipitate out at typical fuel operating temperatures. The drive for segregation is attributed to the increased stability of the solid solution with the ejection of Mo and Ru. When Tc is included in the system, a single phase hexagonal solid solution is expected to form for a wider range of compositions. Furthermore, when cooled below 700 ºC, this single phase solid solution is predicted to transition to a partially ordered structure. Future studies using the Tc-absent analogue will need to take these structural and chemical deliberations into consideration.

Keywords: order–disorder phenomena, density functional theory (DFT), metallic fission product, high-entropy alloy

1. Introduction

When UO_2 nuclear fuel is irradiated to high burn-up, small metallic precipitates containing Mo, Pd, Rh, Ru and Tc are known to form. These are often referred to as the *epsilon phase*, *five metal particles* or, as will be henceforth referred to here, the *metallic fission product* (MFP) – although it is acknowledged that other metallic fission products have been observed, such as $(U,Pu)(Rh,Pd)_3$ [1]. Precipitation of MFPs affect the distribution of other fission products in the UO_2 matrix and oxide secondary phases such as $(Ba,Sr)(Zr,Mo)O_3$ *grey phase*, which in turn impacts on the chemical, microstructural and thermal properties of the fuel pellet [2, 3].

Abbreviations: HEA – High-entropy alloy, SPHEA – Single phase high-entropy alloy, MFP – Metallic fission product, MFP-noTc – Metallic fission product without Tc

Understanding the stability of MFPs as a function of composition will provide valuable information for the development of UO_2-based nuclear fuel with improved performance.

A considerable body of research has been produced regarding the stability and composition of MFPs [1, 4-6]. Due to the inherent complications of dealing with radioactive Tc, previous experimental studies [1, 4, 5] have often made the approximation that the chemical similarity of Tc and Ru will allow for the omission of Tc from the melt and that this system would still be indicative of the MFP. The resulting quaternary Mo-Pd-Rh-Ru system, also a subject of the current work, is henceforth referred to as the MFP-noTc (metallic fission product without Tc).

In our previous publication [21] we suggest that MFPs may fall under the broad term of a high-entropy alloy (HEAs). HEAs represent a largely unexplored area in the field of alloy design and discovery and have been a subject of increasing attention since their classification [7, 8]. The definition of HEAs varies in the literature; in this study we make a distinction between a generic HEA system and a single phase HEA (SPHEA). Both are defined as alloys with four or more principal components. The former is labelled a HEA regardless of resultant crystal/micro-structure, but the latter must be able to form a single phase solid solution below the solidus. Due to the development of quantitative methods to predict SPHEA formation [9-12] substantial progress has been made in the discovery of novel systems. However, there is still uncertainty regarding the nature of the atomic arrangements within the solid solutions. It is often assumed that complete disordering across all lattice sites occurs due to the drive of configurational entropy but suggestions of partial ordering have recently been made [13-15]. In view of the recent advances in the field of SPHEAs, we have found that MFPs might be placed into the SPHEA category [5, 16] (see Figure 1), making it one of the few hexagonal SPHEAs reported in the literature [17, 18]. In the current work we apply methods developed for SPHEA to investigate the stability, partitioning and partial ordering of the MFP and MFP-noTc systems as a function of temperature and composition.

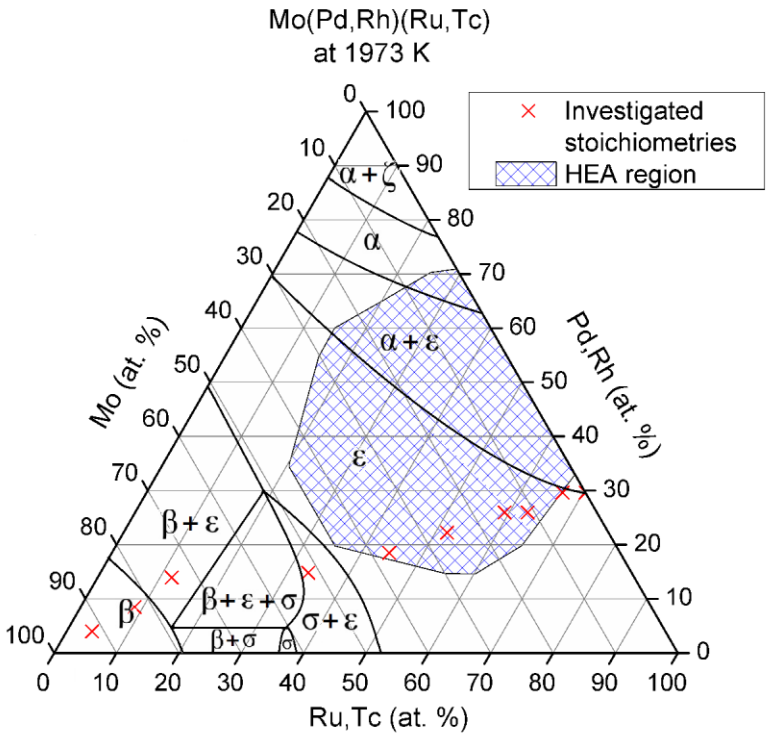


Figure 1. Pseudo-ternary phase diagram of Mo(Pd,Rh)(Ru,Tc), modified from Ref. [1] where (Pd, Rh) and (Ru, Tc) are thought to be sufficiently chemically similar to be interchangeable to approximate the ternary form of the phase diagram. The shaded region represents compositions that are classified as a HEA following the definition provided in [12]. Red crosses are compositions investigated in this study.

2. Methodology

Static *ab-initio* atomic scale simulations based on density functional theory (DFT) were performed with the Vienna Ab initio Simulation Package (VASP) [19, 20] and benchmarked with experimental data from past examination of irradiated nuclear fuel. Pure body-centred cubic (BCC) Mo, face-centred cubic (FCC) Pd and Rh, and hexagonal close-packed (HCP) Ru and Tc were converged independently. Brillouin zone sampling was carried out with a *k*-point density of ~0.035 $Å^{-1}$ and Methfessel-Paxton smearing of 0.125 eV, yielding suitably converged results (<$1x10^{-3}$ eV/unit cell). Simulations were performed under constant pressure and no symmetry was enforced. Projector-augmented wave pseudopotentials [21] with the maximum number of valence electrons (provided within the VASP package version 5.2.12) were used in conjunction with the generalised gradient approximation exchange-correlation functional of Perdew-Burke-Ernzerhof (GGA-PBE) [22]. Spin-polarisation effects were included. The energy convergence criterion for atomic relaxation was set to 10^{-4} eV for all calculations.

The modelled systems included 54 and 48 atom supercells for the disordered and partially ordered systems, respectively. These sizes have been shown to be sufficient to achieve convergence in total energy [13, 23]. The elements in the partially ordered structures with *Pmma* symmetry were designated lattice sites according to the MoRh intermetallic and the remaining elements were grouped according to Kleykamp et al.'s pseudo-ternary phase diagram [1] with (Rh, Pd) sharing the Wycoff *2f* and (Mo, Ru, Tc) on the *2e* lattice site. The method for modelling, calculating entropy and simulating the systems' associated X-ray diffraction (XRD) patterns are detailed in previous studies [15, 24] where each supercell was generated (pseudo-randomly) ten times.

3. Results

To align the compositional variation of the MFP to that of experiment [5, 24], the stoichiometry was kept as close as possible to $Mo_xPd_9Rh_9Ru_{28}Tc_{14}$, where *x* varied to an equivalent of 0 – 87 at. % (red crosses in Figure 1). The Mo content in the MFP is inversely related to the burn-up of the fuel; the decrease in content is due to Mo segregation into *grey phases* as free oxygen becomes available due to fission processes [1, 5]. The σ phase, that is known to form within the Mo-Ru binary system, has also been observed in Kleykamp's pseudo-ternary Mo-(Pd,Rh)-Ru phase diagram [4] (Tc omitted) at compositions with Mo > 50 at. % (at 1973 K).

The drive for precipitation of the σ phase from the solid solution (forming σ-Mo_5Ru_3 + solid solution) was assessed in both the MFP and MFP-noTc. This was done by removing Mo and Ru from solid solution in a ratio of 5:3 (representing ~15% of the atoms in the 54 atom supercells), example reaction:

$$(Mo_6Pd_7Rh_7Ru_{23}Tc_{11})_{ss} \rightarrow (Mo_1Pd_7Rh_7Ru_{20}Tc_{11})_{ss} + (Mo_5Ru_3)_{\sigma} \quad (1)$$

The resulting solid solution is rescaled to a new composition to maintain 54 atoms (see supplementary methods and Table S1) and the σ phase formation enthalpy was calculated separately.

Figure 2 shows the stability of the single phase solid solution (solid line) and dual phase σ + solid solution (dashed line) as a function of Mo content at 1973 K. In agreement with Kleykamp's experimental observations, it was found that MFP-noTc (Figure 2a) de-stabilises into a dual phase σ + solid solution for Mo contents above 45 at. %.

Importantly, when Tc is included in the system (Figure 2b), the σ phase is predicted to only precipitate at very high Mo contents which is representative of low burn-up fuel conditions

when the total inventory of fission products in the fuel is very low. Note that at this point, the composition is far from that of a HEA system, and it is therefore not surprising that the formation of an intermetallic compound is thermodynamically favourable.

Due to the difference in expected behaviours between the system containing Tc and the system omitting Tc, these predictions suggest that the use of the MFP-noTc as a surrogate for the MFP-Tc system is limited as the secondary phases present will interact with other fission products and vary the mechanical behaviour of the metal system [25]. As such, we suggest that the MFP-noTc surrogate only be used for simulation of high-burnup situations where the Mo content of the MFP is lower. For low-burnup situations, an alternative alloying addition is required – possibly Re which mimics the electronic behaviour of Tc more reliably compared to Ru [26].

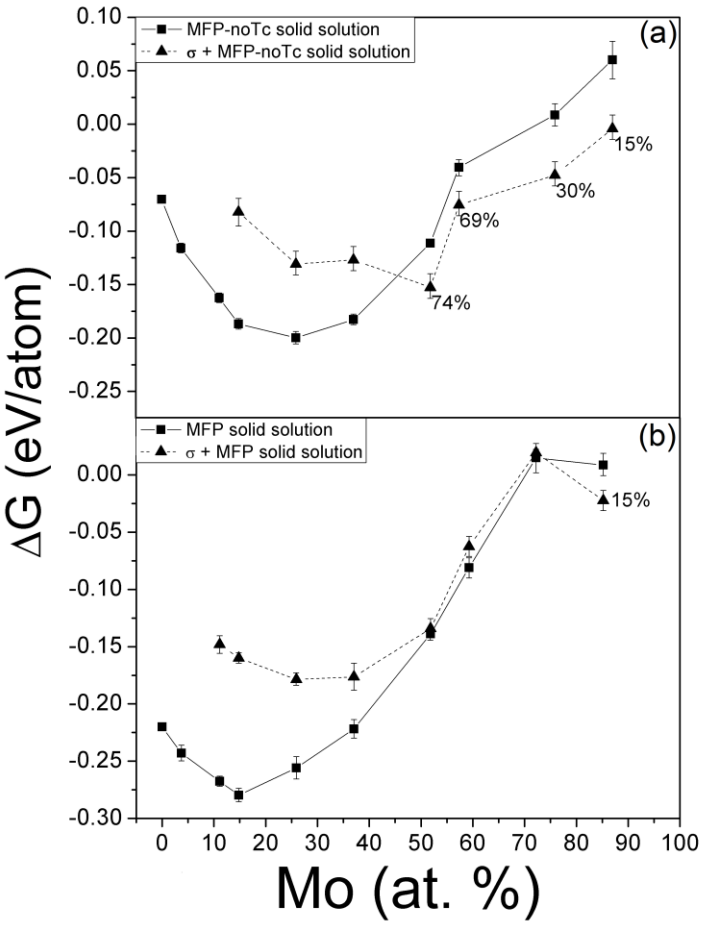


Figure 2. The Gibbs free energy at 1973 K for the (a) MFP-noTc and (b) MFP single phase solid solution (square) and dual phase σ + solid solution (triangle) with change in Mo content. The volume percent of σ phase, predicted to form, labels the relevant data points. Standard deviation in energy between supercells are denoted by error bars.

Regarding the solid solution phase, it has been assumed that the MFP adopts a fully disordered HCP solid solution (ε phase). However, when considering the Mo-Rh binary phase diagram (Figure 3) an ordered MoRh intermetallic with *Pmma* symmetry is observed – very similar to the HCP atomic arrangement. When comparing the difference in average enthalpy of formation between the fully disordered $P6_3/mmc$ and partially ordered *Pmma* solid solution, according to Figure 4, we find a relatively significant enthalpy difference. This phenomenon cannot easily be identified through thermodynamic treatments that extrapolate from lower order binary and ternary systems as done by Kaye et al. [6].

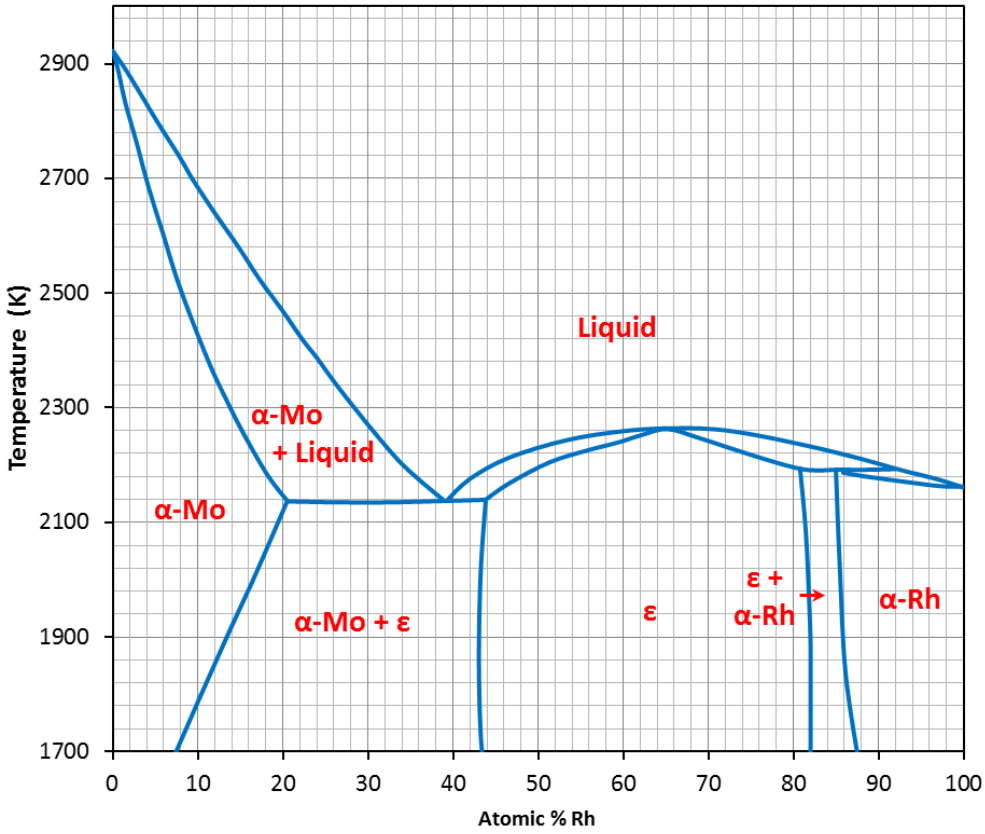


Figure 3. Mo-Rh binary phase diagram, modified from [27].

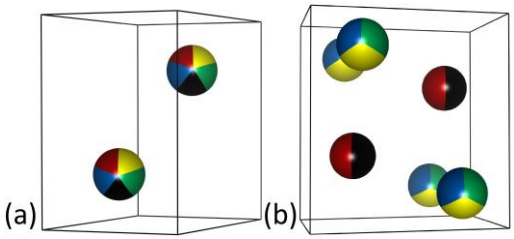


Figure 4. (a) The fully disordered HCP unit cell and (b) the partially ordered *Pmma* unit cell whereby the Wyckoff 2e position is occupied by Mo (green), Ru (yellow) and Tc (blue) and 2f position is occupied by Pd

(red) and Rh (black). In an excess of Mo, the remaining Mo is also included on the 2f position in this investigation.

Figure 5 assesses the drive for the MFP to form the partially ordered phase (ε') over the fully disordered HCP solid solution. It is found that for all compositions containing Mo (ie. $x > 0$ at. %), the partially ordered system exhibits a lower (more favourable) formation enthalpy. When temperature effects are included by means of configurational entropy [28], we observe that the MFP may undergo a transition from partially ordered ε' to fully disordered ε (a tentative phase boundary has been suggested in Figure 5). This concept, has similarities to that of the B2-like partial ordering found in the Mo-Nb-Ta-W [14] and Al-Co-Cr-Fe-Ni system [15] and $L1_2$ partial ordering in the Co-Cr-Fe-Ni system [13]. It should be noted that other forms of entropy (vibrational, electronic and magnetic) will influence the relative stabilities between two different phases. However, the comparison is between phases with the same crystal structure, very similar chemical composition, and no magnetic ordering. We therefore assume electronic and vibrational contributions are of very similar magnitude and magnetic effects may be discounted entirely.

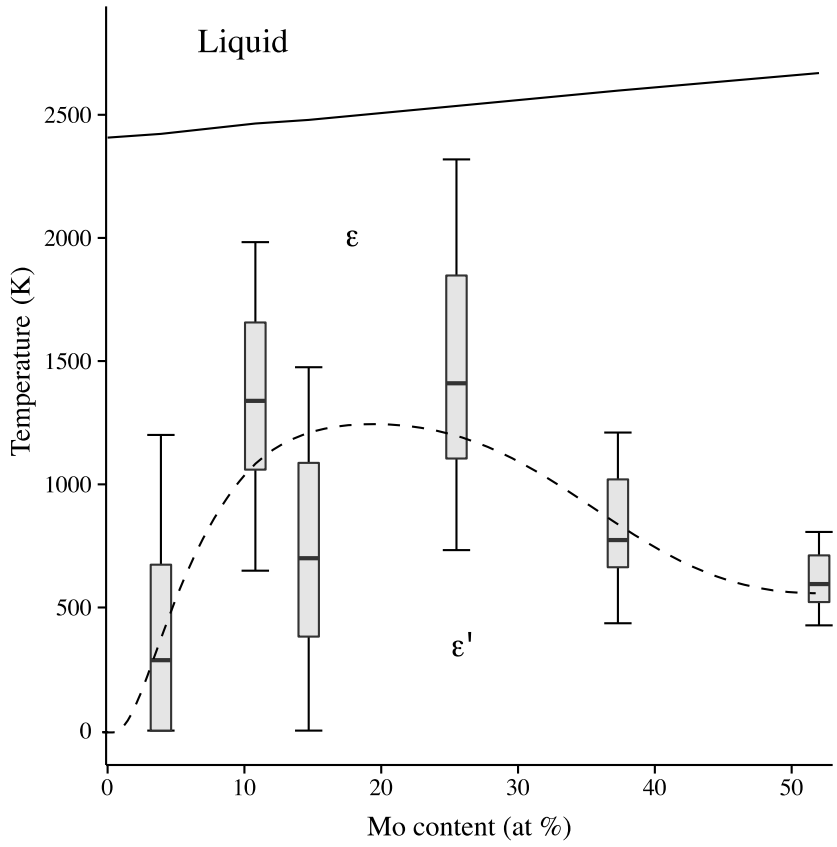


Figure 5. The phase diagram of $Mo_xPd_9Rh_9Ru_{28}Tc_{14}$ where x is varied from 0 – 50 (at %) with the temperature range between upper and lower quartile for transition temperatures of the system (box plots) from a partially ordered (ε' phase) to fully disordered (ε phase) HCP slid solution. The median values are represented as the mid-

points within the box plots and error bars denote the standard deviation. A dashed line is included as a tentative phase transformation boundary and the melting temperature (solid line) is estimated by the rule of mixtures [29].

4. Discussion

The results of this investigation suggest that the addition of Tc has a significant stabilising effect on the single-phase solid solution, and this should be taken into consideration when the MFP-noTc is used as to model the MFP. Interestingly, when assessing the contributions to the drive for precipitation; the σ-Mo_5Ru_3 exhibits a degree of disorder but all configurations have a relatively weak formation enthalpy. The lowest energy configuration (as found by Grånäs et al. [30]) was calculated to be 1.7×10^{-2} eV/formula unit (1.9×10^{-2} eV/formula unit) at 0 K in this study. Experimentally, the formation enthalpy has been measured as -8.1×10^{-5} eV/formula unit at 1760 K [31]. Comparing this to the difference in energy between the solid solutions before and after the removal of Mo and Ru (which can be as favourable as $-7.7 \pm 0.4 \times 10^{-2}$ eV/formula unit) we can conclude that it is the increase in stability of the solid solution that drives precipitation, not the heat of formation of the precipitate itself.

When assessing the different configurations of the solid solution, the fully disordered arrangement is more favorable when '*x*' is 0 at. % (ie. no Mo) for all temperatures. However, when Mo is included, at low temperatures (where the enthalpy contribution may dominate over configurational entropy), the partially ordered ε' phase becomes more stable than the fully disordered ε phase. The entropy difference that drives the disordering ranges from 1.17×10^{-5} – 2.23×10^{-5} eV/atom/K. The order-disorder transition temperature can be estimated by equating the free energy $(\Delta H - T\Delta S)$ of both phases, where ΔH is the enthalpy of mixing (determined by DFT), T is temperature and ΔS is the configurational entropy, of the two phases for each given composition [15]. Other thermal effects, such as vibrational entropy, are assumed to be similar between the two phases and thus largely cancel out – an assumption that generally valid unless there is a change in material state [32].

At the annealing temperature of 1973 K used by Kleykamp and Paschoal et al. [4] most stoichiometries are predicted to exhibit complete disorder, with some uncertainty in the composition region between Mo contents of ~11 – 25 at.%. Importantly, the XRD patterns of the partially ordered and disordered phases (Figure 6) display subtle differences, with the ordered structure displaying very low intensity peaks and small shifts in d-spacing that may be

missed in conventional laboratory X-ray experiments due to the effects of crystal distortion [33], noise and similarities in X-ray scattering factors [34].

Fission product segregation and therefore fuel behaviour will be impacted by the phases present in the nuclear fuel [3, 24]. Our simulations show that MFP-noTc does not fully simulate the behaviour of the expected Tc containing MFP. If these predictions can be verified via experimental means, the next step for development would be to suggest an alternative alloying addition to replace Tc that would mimic the behaviour of the alloy.

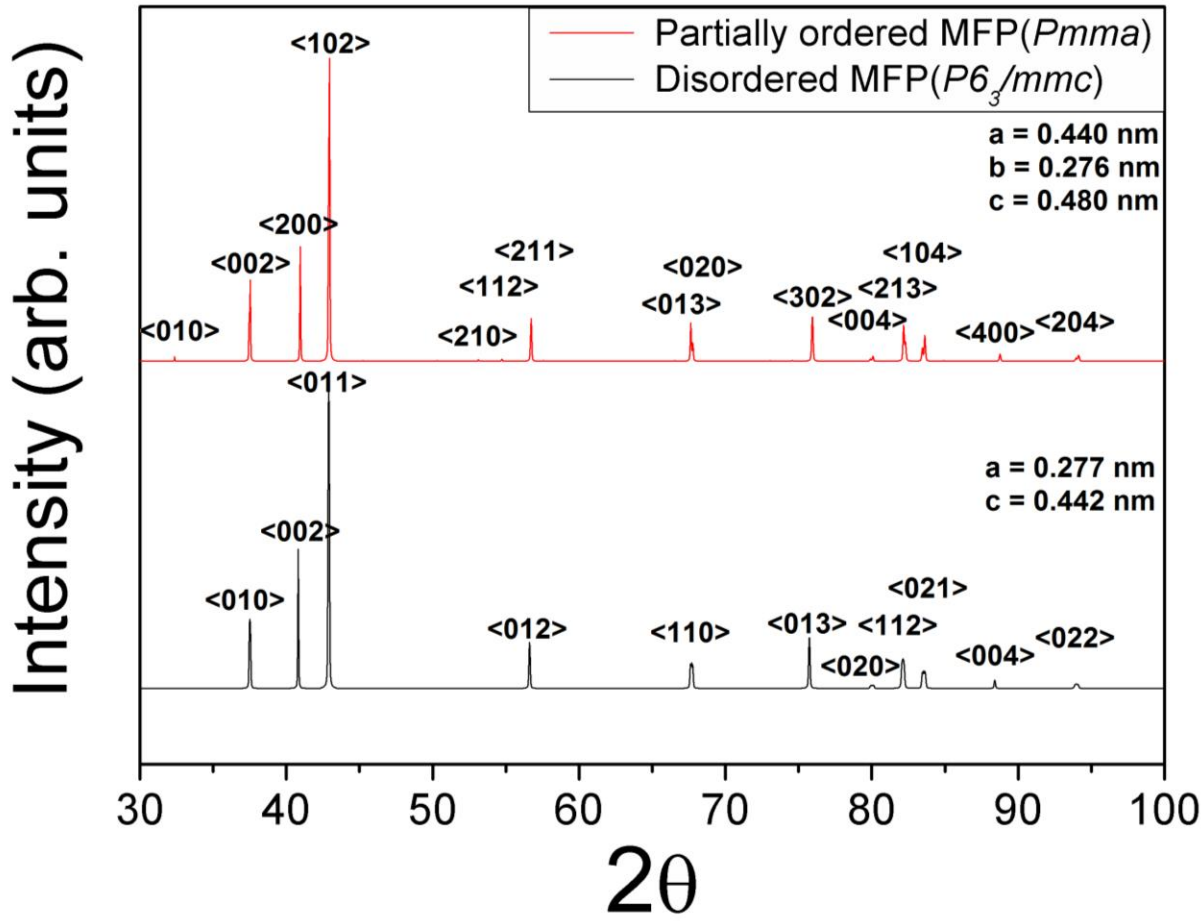


Figure 6. Comparison of simulated XRD patterns using CuKα radiation between partially ordered (red) and fully disordered (black) MFP with the $Mo_{21}Pd_9Rh_9Ru_{28}Tc_{14}$ stoichiometry.

5. Conclusions

From these findings, it is possible that the MFP ε phase region is larger compared to the MFP-noTc reported by Kleykamp [1], which would affect material properties and interaction (accommodation and solubility) with other fission products in the UO_2 fuel. Furthermore, the significant change in behaviour, in terms of stability and structure, between the MFP and MFP-noTc could potentially mean that past assumption of their equivalence is incorrect.

At temperatures below ~2000 K the ε phase may adopt a partially ordered crystal structure. This phenomenon might require long anneal times to reach the equilibrium state [34, 35] but could be reasonably achieved within the reactor fuel lifetime. Nevertheless, the effect of radiation damage effects may act to mix the alloy, preventing the ordered system from evolving fully.

Current models that are used to predict and classify SPHEAs generally assume the formation of the intermetallic phases are due to their largely negative enthalpy of formation [9, 36, 37]. However, in some cases, the intermetallic compounds in HEA systems have a very weak drive for formation in terms of formation enthalpy. Examples are the V_2Zr Laves phase and the Mo_5Ru_3 σ phase which both have a positive formation enthalpy at 0 K [30, 38]. As shown here, the relative stabilities of the solid solutions after segregation of elemental species must also be considered in the drive for SPHEA stability.

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