Isothermal Transformation Kinetics in Uranium Molybdenum Alloys

Master Thesis in Physics
submitted by

Steffen Säubert

September 2013
Isothermal Transformation Kinetics
in Uranium Molybdenum Alloys

This Master Thesis has been carried out by Steffen Säubert at the
Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)
under the supervision of
Prof. Dr. Winfried Petry
Chair of Functional Materials E13
Physics Department, Technische Universität München
Abstract

Exposing uranium-molybdenum alloys (UMo) retained in the \( \gamma \)-phase to elevated temperatures, transformation reactions set in during which the \( \gamma \)-UMo phase decomposes into the thermal equilibrium phases, i.e. \( \text{U}_2\text{Mo} \) and \( \alpha \)-U. Since \( \alpha \)-U is not suitable for a nuclear fuel exposed to high burn-up, it is necessary to retain the \( \gamma \)-UMo phase during the production process of the fuel elements for modern high performance research reactors.

The present work deals with the isothermal transformation kinetics in U8wt.-%Mo alloys for temperatures between 400 \( ^\circ \)C and 525 \( ^\circ \)C and annealing durations of up to 48 h. Thereby, annealed samples were examined at room temperature using either high-energy X-ray diffraction (HE-XRD) or neutron diffraction. The obtained diffraction patterns were analysed with Rietveld refinement and, hence, the phase composition after thermal treatment was determined.

Moreover, in-situ annealing studies using neutron diffraction were performed. These measurements delivered the onset of phase decomposition by observing the peak intensities as a function of annealing time, i.e. peak growth curvatures.

While for temperatures of 425 \( ^\circ \)C and 400 \( ^\circ \)C the start of decomposition is delayed, for higher temperatures the first signs of transformation are already observable before 3 h of annealing. Not only the onset of phase decomposition at lower temperatures is delayed, but also the transformation itself is very sluggish. The typical C-shaped curves in a TTT-diagram for the start and end of phase decomposition, respectively, could be determined in the observed temperature regime. Therefore, a revised TTT-diagram for U8wt.-%Mo between 400 \( ^\circ \)C and 525 \( ^\circ \)C and of up to 48 h is proposed.
Zusammenfassung

Setzt man Uran-Molybdän Legierungen (UMo) in der $\gamma$-Phase erhöhten Temperaturen aus, kommt es zu Reaktionen, die die $\gamma$-UMo Phase zersetzt. Das thermische Gleichgewicht ist eine Mischung der Phasen $U_2Mo$ und $\alpha-U$. Uran in der $\alpha$-Phase ist nicht für ein Brennmaterial geeignet, welches hohen Abbränden ausgesetzt ist. Daher ist es notwendig die $\gamma$-Phase während des Herstellungsprozesses eines Brennelements für Hochleistungsforschungsreaktoren beizubehalten.


Des Weiteren wurden in-situ Messungen mit Neutronendiffraktion durchgeführt. Mit Hilfe dieser Messungen wurde der Beginn der Phasenumwandlung ermittelt, indem die Intensität der Peaks als Funktion der Ausglühzeit, sogenannte Peakwachstumskurve, ermittelt wurde.

Während für Temperaturen von 425°C und 400°C die Zersetzung verspätet beginnt, sind bei höheren Temperaturen bereits vor 3h erste Zeichen der Transformation erkennbar. Für die niedrigeren Temperaturen ist nicht nur der Zersetzungsbeginn verzögert, sondern auch der Transformationsprozess selbst ist sehr träglich. Im beobachteten Temperaturbereich wurden die typischen C-förmigen Kurven des TTT-Diagramms ermittelt. Somit wird ein überarbeitetes TTT-Diagramm für U8wt.-%Mo im Bereich zwischen 400°C und 525°C und für bis zu 48h vorgestellt.
Table of Contents

6.2.1 X-Ray Diffraction ........................................... 38
6.2.2 High-Energy X-Ray Diffraction .............................. 38
6.2.3 Neutron Diffraction (SPODI) ............................... 39
6.3 In-Situ Annealing Measurements ............................... 42
6.3.1 Neutron Diffraction (STRESS-SPEC) ....................... 42

III Results and Discussion ........................................ 45
7 Crystallographic Phase Analysis via Rietveld Refinement .... 47
  7.1 Data Analysis .................................................. 47
  7.2 Initial U8wt.-%Mo Phase ....................................... 48
  7.3 High-Temperature Reactions – 475°C and 500°C ......... 50
      7.3.1 Isothermal Studies at 475°C ......................... 50
      7.3.2 Isothermal Studies at 500°C ......................... 53
  7.4 Intermediate-Temperature Reactions - 400°C, 425°C and 450°C 56
      7.4.1 Isothermal Studies at 450°C ......................... 56
      7.4.2 Isothermal Studies at 425°C ......................... 59
      7.4.3 Isothermal Studies at 400°C ......................... 61

8 Phase Decomposition Measurements During In-Situ Annealing .... 63
  8.1 Data Analysis .................................................. 63
  8.2 High-Temperature Reactions - 475°C, 500°C and 525°C .... 65
      8.2.1 Isothermal In-Situ Annealing Studies at 500°C .... 65
      8.2.2 Isothermal In-Situ Annealing Studies at 525°C .... 68
      8.2.3 Isothermal In-Situ Annealing Studies at 475°C .... 69
  8.3 Intermediate-Temperature Reactions - 450°C and 425°C .... 72
      8.3.1 Isothermal In-Situ Annealing Studies at 450°C .... 72
      8.3.2 Isothermal In-Situ Annealing Studies at 425°C .... 73
  8.4 High-Temperature Phase Transition .......................... 76
  8.5 Coefficient of Thermal Expansion for γ-UMo .......................... 77

9 Isothermal Transformation Diagram for U8wt.-%Mo ............ 79
  9.1 Contribution of the Individual Methods ..................... 79
  9.2 Comparison with Previous Results .......................... 85

IV Conclusion ......................................................... 87
10 Summary and Outlook ............................................ 89
  10.1 Summary ..................................................... 89
  10.2 Outlook ..................................................... 90
      10.2.1 High-Temperature Phase Transition via Differential Scanning Calorimetry 90
      10.2.2 Additional Data Obtained by In-Situ Annealing Studies .................. 90
      10.2.3 Complementing the TTT-Diagram for U8wt.-%Mo .......................... 92

V Appendix .............................................................. i

VI
# Table of Contents

A  Chemical Analysis of the UMo-Ingot by AREVA-CERCA ........................................ iii

B  NIST Standard Certificates .................................................................................. v

C  Tables

  C.1  Data on Phase Decomposition Measurements During In-Situ Annealing .......... ix

Indices

  List of Figures .......................................................................................................... xi
  List of Tables ........................................................................................................... xv
  Bibliography ............................................................................................................ xvii
  Acknowledgement ..................................................................................................... xxi
  Eidesstattliche Erklärung ........................................................................................... xxiii
  Revisions .................................................................................................................. xxv
CHAPTER 1

Motivation

The Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) is a research neutron source located in Garching, Germany. Since the year 2004 the research reactor provides neutrons for fundamental and applied science, industry and medical applications. Due to a broad selection of secondary sources for the neutrons at the FRM II, a large variety of different instruments are operated. The neutron spectrum covers the cold neutrons with a low energy of about 5 meV, the thermal neutrons with $E = 25$ meV, the hot neutrons in the energy range 0.1 eV to 1 eV and the fission neutrons with energies around 2 MeV. Moreover, an ultracold neutron source with neutron energies below 250 neV will be installed at beam tube SR4 in the near future [1].

With an undisturbed thermal neutron flux of $8 \cdot 10^{14}$ $n/cm^2s$, what corresponds to a disturbed thermal neutron flux of $6.4 \cdot 10^{14}$ $n/cm^2s$, and a thermal power of only 20 MW, the FRM II has the highest flux-to-power ration worldwide. The FRM II is a light water cooled, heavy water reflected compact core reactor driven by a single fuel element. Its geometry is depicted in Figure 1.1a. The element contains 8.1 kg uranium with an enrichment of 93% which is therefore considered to be highly enriched uranium (HEU) fuel. The fuel element, shown in Figure 1.1b, consists of 113 involute shaped fuel plates which are arranged cylindrically. Currently, the fuel is uranium silicide powder ($U_3Si_2$) dispersed in an aluminium matrix at a maximum density of $3.0\, \text{gU/cm}^3$ and cladded by an aluminium alloy (AlFeNi) which keeps the fission products enclosed and provides a good heat dissipation. [1]

However, highly enriched uranium has increasingly become a political topic of discussion in the national and international context. Thus, efforts are made to reduce the amount of HEU in the civilian nuclear fuel cycle. FRM II supports these international efforts with a large, dedicated working group. It is even part of the nuclear license of FRM II to reduce the enrichment to a lower enriched fuel element, provided that a suitable fuel exists. There are two possibilities to achieve this requirement:

1. Reconstruction of the core geometry and a new arrangement of the fuel element. This would yield a low enrichment at the expense of huge financial and technical challenges, which are accompanied by several licensing issues and very long shut-down times. [2, 3]

2. An all-new fuel type with higher uranium density which fits the current core geometry. Thereby, a comparably higher enrichment would be required. [3]

Due to the non-justifiable efforts and risks associated with a core reconstruction, a new fuel is the only practicable solution. To be considered as suitable, the new fuel needs to meet some general conditions which form the main conversion criteria [3]:

\begin{itemize}
  \item[1.] Reconstruction of the core geometry and a new arrangement of the fuel element. This would yield a low enrichment at the expense of huge financial and technical challenges, which are accompanied by several licensing issues and very long shut-down times. [2, 3]
  \item[2.] An all-new fuel type with higher uranium density which fits the current core geometry. Thereby, a comparably higher enrichment would be required. [3]
\end{itemize}
1. Motivation

(a) Concept characteristics of the Frm II whereas the red rectangle shows the place of the cylindrical fuel element [1]

(b) Cylindrical fuel element with an inner radius of 118 mm, an outer radius of 243 mm and a height of 700 mm - with its packaging it is 1.3 m high [1]

*Figure 1.1: (a) the cross section through the reactor core at the Frm II shows the geometry, the new fuel element needs to fit; (b) the current fuel element with its involute shaped 113 fuel plates*

- Only marginal losses in the neutron flux and quality are acceptable.
- The cycle length must be at least today’s value of 60 days.
- No compromises regarding the safety of the reactor.
- The conversion must be economically feasible.

Currently, the highly enriched fuel has an uranium density of $3 \text{ g/cm}^3$ in the center of the plates and $1.5 \text{ g/cm}^3$ in the outer rim. To achieve equivalent neutron fluxes and quality with a lower enriched fuel, the uranium density needs to be increased significantly. Whereas a conversation to a currently existent fuel leads to non-acceptable performance losses [4], the straight forward conversion to a LEU fuel would require an uranium density of $40 \text{ g/cm}^3$ which exceeds the density of pure metallic uranium [5], according to [6]. With a reduction from HEU to medium enriched uranium (MEU) with 30% $^{235}\text{U}$, an uranium density of $8 \text{ g/cm}^3$ would be sufficient, which is close to the very limit for dispersed fuels [2].

A point to consider by choosing a new fuel element is the phase behaviour of the fuel under thermal treatment and irradiation. Since, for example, the orthorhombic $\alpha$-phase, present in pure uranium metal, is mechanically unstable under irradiation to high burn-up, uranium
alloys are preferred over pure uranium. Alloying uranium aims to stabilize the cubic $\gamma$-phase of uranium, which is the only uranium phase suitable for irradiation. Furthermore, during elevated temperatures, reactions of the fuel with the aluminium matrix happen much faster when the $\alpha$-phase is present [7]. The most promising future fuel for the FRM II is an uranium molybdenum alloy (UMo) that can achieve uranium densities of up to 15 g/cm$^3$ in its pure monolithic form. Advantages of this alloy is the preservation of the $\gamma$-phase of uranium at room temperature and a high uranium density. UMo as a disperse fuel would require 30% $^{235}$U whereas for the monolithic solution 27% enrichment would be sufficient [3].

However, during the production process of the fuel elements as well as during the operation inside the reactor core, temperatures above the room temperature are present. Depending on the temperature, on which the fuel is treated, transformation reactions set in and the $\gamma$-UMo phase starts to decompose into the thermal equilibrium micro-structures, i.e. $\text{U}_2\text{Mo}$ and $\alpha$-U. The longer a fuel is kept on elevated temperatures, the stronger the decomposition will be. These *Isothermal Transformation Kinetics of Uranium Molybdenum Alloys* are the topic of this thesis. An alloy with a molybdenum content of 8wt.-% is considered a good compromise between the stabilization of the $\gamma$-phase and a high uranium density. Therefore, this alloy is in the focus of this thesis.
Part I

Scientific Background
This chapter introduces the different phases and phase transitions occurring in pure uranium as well as in uranium alloys and, therefore, will show the necessity of alloying uranium for the stabilization of the $\gamma$-phase. This thesis uses the phase nomenclature introduced by Lehman and Hills in 1960 [8]. Crystallographic parameters of the different phases in uranium and uranium alloys are summarised in Table 2.1.

Table 2.1: Crystallographic parameters of the different phases in uranium and uranium-molybdenum

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>Crystal structure</th>
<th>Space group</th>
<th>Lattice constant $[\text{Å}]$</th>
<th>Angle $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>$\alpha$</td>
<td>orthorhombic</td>
<td>Cmcm</td>
<td>$a = 2.8539$</td>
<td>$b = 5.8678$</td>
</tr>
<tr>
<td>U</td>
<td>$\beta$</td>
<td>tetragonal</td>
<td>P42/mmm</td>
<td>$10.7589$</td>
<td>$10.7589$</td>
</tr>
<tr>
<td>U</td>
<td>$\gamma$</td>
<td>cubic</td>
<td>Im-3m</td>
<td>$3.472$</td>
<td>$3.472$</td>
</tr>
<tr>
<td>UMo</td>
<td>$\alpha'$</td>
<td>orthorhombic</td>
<td>Cmcm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UMo</td>
<td>$\alpha''$</td>
<td>monoclinic</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UMo</td>
<td>$\gamma^o$</td>
<td>tetragonal</td>
<td>P4/nbm</td>
<td>$2a_\gamma$</td>
<td>$2b_\gamma$</td>
</tr>
<tr>
<td>U$_2$Mo</td>
<td>$\gamma'$</td>
<td>tetragonal</td>
<td>I4/mmm</td>
<td>$3.427$</td>
<td>$3.427$</td>
</tr>
</tbody>
</table>

2.1 Pure Uranium

The pure uranium metal occurs in three allotropes between room temperature and its melting point at 1132°C: $\alpha$-phase, $\beta$-phase and $\gamma$-phase.

$\alpha$-phase:

The $\alpha$-phase is stable for temperatures up to 667°C and possesses four atoms per unit cell in its orthorhombic structure shown in Figure 2.1a. The space group symbol is Cmcm. The lattice parameters at room temperature are

\[
a = 2.8539 \text{ Å} \quad b = 5.8678 \text{ Å} \quad c = 4.9554 \text{ Å}
\]

with thermal expansion coefficients of

\[
\alpha_a = 36.1 \cdot 10^{-6} \frac{1}{\text{K}} \quad \alpha_b = -9.3 \cdot 10^{-6} \frac{1}{\text{K}} \quad \alpha_c = 33.0 \cdot 10^{-6} \frac{1}{\text{K}}
\]
2.1. Pure Uranium

where the thermal expansion coefficients for the lattice parameters are calculated by Equation 2.4, whereby the calculation is discussed later in Chapter 2.4. A striking aspect is that the lattice parameters $a$ and $c$ increase with temperature while the $b$ parameter decreases. [9]

$\beta$-phase:
The $\beta$-phase is present for temperatures between 667°C and 775°C. This tetragonal phase has 30 atoms per unit cell and is depicted in Figure 2.1b. The space group symbol is P42/mnm and the lattice parameters at 682°C are

\[
a = b = 10.7589 \, \text{Å} \quad c = 5.6531 \, \text{Å}
\]

with thermal expansion coefficients of

\[
\alpha_a = \alpha_b = 21.9 \cdot 10^{-6} \frac{1}{\text{K}} \quad \alpha_c = 18.4 \cdot 10^{-6} \frac{1}{\text{K}}
\]

where the thermal expansion coefficients for the lattice parameters again are calculated by Equation 2.4. [9]

$\gamma$-phase:
The $\gamma$-phase exists for temperatures above 775°C up to the melting point at 1132°C. This high temperature phase has a body-centered cubic structure shown in Figure 2.1c and the space group symbol Im-3m. The lattice parameter at 787°C is [9]

\[
a = b = c = 3.5335 \, \text{Å}
\]

Before these results, in 1974 Yakel [10] reviewed X-ray diffraction studies where uranium-zirconium alloys were measured and the measured data extrapolated to zero solute which led to the estimated lattice parameters

\[
a = b = c = 3.534 \, \text{Å at 800°C} \quad a = b = c = 3.472 \, \text{Å at room temperature}
\]

and hence an estimated thermal expansion coefficient of

\[
\alpha_a = \alpha_b = \alpha_c = 21.6 \cdot 10^{-6} \frac{1}{\text{K}}
\]

The $\alpha$-phase is mechanically unstable under irradiation to high burn-up as well as under thermal cycling and therefore not suitable for being present in a nuclear fuel. Important in explaining these behaviours is the above-mentioned anisotropic expansion of the lattice parameters. There are two processes causing radiation damage in uranium. First, the displacement of atoms by elastic collision with neutrons and fission fragments. Second, chemical and mechanical damage due to the very existence of fission products within the fuel. If the specimen is highly textured and fine grained, very strong changes in the dimension are observable as can be seen in Figure 2.2a. As for thermal cycling two different processes can explain the deformation of an uranium sample. Both of them are involving grain boundaries. First, a grain boundary flow between two adjacent grains of differing thermal expansion. Second, stress relaxation in one of these grains by plastic deformation. Such a thermal ratcheting can only work if the thermal expansion of the specimen is anisotropic like it is the case for $\alpha$-U [12, 13]. Therefore, thermal cycling
2. Phase Behaviour of Uranium and Uranium Alloys

Figure 2.1: Allotropes in which the pure uranium metal can occur – (a) shows the orthorhombic α-phase stable for temperatures up to $667^\circ C$; (b) shows the tetragonal β-phase stable for temperatures between $667^\circ C$ and $775^\circ C$; (c) shows the body-centered cubic γ-phase stable in the high temperature regime above $775^\circ C$ up to the melting point of $1132^\circ C$. [11]
2.2. Uranium Alloys

(a) A: initial size of the uranium rod; B: growth of the rod by irradiation

(b) Thermal cycling growth from 5 cm to 30 cm by 300 cycles from 50 °C to 500 °C
(scale on picture is in inch)

Figure 2.2: Damage in fine grained highly textured α-uranium due to irradiation (a) [14] and thermal cycling (b) [12], respectively

damage, as can be seen in Figure 2.2b, only occurs in specimens with grain boundaries, i.e. polycrystalline samples, whereas radiation damage can also occur in single crystals. These effects are not subject of this thesis, however, it is necessary to understand them as a motivation of it. Further information can be found in Physical Metallurgy of Uranium, Chapters 11-12 [12], where, in 1958, Holden compared radiation and thermal cycling growth.

2.2 Uranium Alloys

Since it is indispensable for a nuclear fuel element to keep its shape during the production process and the operation inside the reactor core, respectively, it is necessary to mitigate radiation and thermal cycling damage. Therefore, a stable uranium phase needs to be retained inside the fuel element. The best solutions are highly γ-miscible systems which are characterized by stabilizing the high temperature γ-phase of uranium at room temperature [15]. Moreover, the effects of aqueous corrosion and diffusion mechanisms are lower in such alloys as for pure uranium. Beside the preferred γ-phase alloys, it is possible to suppress uranium growth with α-phase alloys. In Figure 2.3 the increased stability of the material by adding zirconium compared to pure uranium is shown. It has been shown by Kittel et al. [16] that alloying additions like zirconium greatly refines the grain size. Moreover, alloying can alter the transformation kinetics of uranium in order to remove preferred orientations by heat treatment. In such an α-phase alloy, the specimen is heated briefly to the γ-phase regime followed by an isothermal annealing. By doing so, the alloy is transformed completely to the α-phase. [17, 18]

The heat treatment for retaining the γ-phase in an alloy is quenching the specimen from the γ-phase. In order to homogenize the γ-phase, annealing in γ-phase temperature regimes is
Figure 2.3: Effect of zirconium additions on the stability of cast uranium irradiated to 0.6 at.-% burn-up [16]
conducted. Many transition elements, e.g. Ti, Zr, Nb, Mo, Ru, Rh, Re, form such a system with a solubility inside \( \gamma \)-uranium higher than 10at.\-%. The choice of an element depends on the one hand on the fact that the \( \gamma \)-phase stabilization increases with the atomic number of the alloying element and on the other hand that the solubility decreases for bigger size difference of the elemental atoms and the uranium atoms. [7, 16]

The required solution for \( \gamma \)-phase stabilization together with a high uranium density makes molybdenum a good candidate for alloying with uranium. The relationship between \( \gamma \)-phase stabilization and uranium density is depicted in Figure 2.4. Therefore, Section 2.3 introduces the physical properties of uranium-molybdenum alloys in more detail.

### 2.3 Uranium Molybdenum

Uranium-molybdenum alloys retain the desired \( \gamma \)-phase of uranium at room temperature for a content of molybdenum between 4.5wt.\-% (10.5at.\-%) and 15.5wt.\-% (31.3at.\-%). If there is less than 4.5wt.\-% Mo, the sample would show U inclusions inside an UMo alloy. For a content higher than 15.5wt.\-%, on the other hand, Mo would be precipitated and form inclusions in the alloy. Figure 2.5 shows the UMo binary phase diagram. For example, this diagram shows that
U8wt.-%Mo at equilibrium conditions and room temperature is a mixture of α-uranium and U₂Mo and at 1000 °C the alloy is in a γ-phase where Mo is dissolved in U, i.e. solid solution. If, on the other hand, a non-equilibrium state is considered like it is the case for an alloy in the γ-phase quenched to room temperature, the resulting phase depends on the content of Mo inside the alloy [10, 20–22]. The sequence of structures at room temperature progresses, as the alloys Mo content is increased, from

$$\alpha \rightarrow \beta \rightarrow \alpha' \rightarrow \alpha'' \rightarrow \gamma^0 \rightarrow \gamma \rightarrow \gamma'$$

whereas, besides the already above-described α- and β-phase, the single phases are characterized as follows:

**α′-phase**: Modification of the α-uranium structure. This distorted α is characterized by the contraction of the b parameter together with an expansion of the parameters a and c. [8, 23]

**α″-phase**: Distortion of the α-phase where, compared to α′, the b parameter is contracted further while a and c are more expanded. Moreover, the phase is changed from an orthorhombic to a monoclinic structure and one angle is slightly increased from the initial 90° to 90.05°– 93°. Which one of the angles depends on the yet unknown space group. [8, 23, 24]

**γ^0-phase**: This phase is a body-centered tetragonal distortion of the γ-phase. Compared to the γ-phase, the lattice parameters a and b are approximately twice as big where \(c_{\gamma^0} \leq c_\gamma\). The
2.3. Uranium Molybdenum

Figure 2.6: Intermetallic compound U\textsubscript{2}Mo; shown is the positions of the uranium (blue) and molybdenum atoms (purple) inside the unit cell [11]

space group is P4/nbm. [20, 21]

\(\gamma'-\)phase: Intermetallic compound of uranium in the highly \(\gamma\)-miscible systems. The \(\gamma'-\)phase, i.e. U\textsubscript{2}Mo and often denoted as \(\delta\)- or \(\epsilon\)-phase, has a tetragonal structure with the space group symbol I4/mmm and is stable in the range of 30 – 35at.-% Mo. The lattice parameters are

\[
a_{\gamma'} \approx b_{\gamma'} \approx 3.427 \text{ Å} \approx a_\gamma \quad c_{\gamma'} \approx 9.834 \text{ Å} \approx 3 \cdot c_\gamma
\]

and therefore similar to the \(\gamma\)-phase. Figure 2.6 shows the lattice structure of U\textsubscript{2}Mo. [10,25]

Besides the content of the alloy, other features also determine the resulting phases at room temperature. In addition, it depends on the cooling rate from the high temperature \(\gamma\)-phase as well as on the temperature the cooling started from. Moreover, the alloying element also plays a role in this sequence and not every phase occurs in all highly \(\gamma\)-miscible uranium alloys.

Except for the stable \(\alpha\)-phase and the also stable intermetallic compounds, i.e. \(\gamma'-\)phases, the phases are metastable and decompose into phases closer to the thermal equilibrium. This decomposition can be induced by different processes like heat treatment or mechanical working. The decomposition of the retained \(\gamma\)-phase under heat treatment will be discussed in more detail in Chapter 3.

As already mentioned above, it is possible to retain the \(\gamma\)-phase at room temperature depending on the content of the alloy. Consider again U8wt.-%Mo, the desired \(\gamma\)-phase is retained after quenching the specimen from the high temperature regime. Moreover, the molybdenum content determines the lattice parameter of the \(bcc\) \(\gamma\)-UMo crystal structure. The three empirical Formulas 2.1 [26], 2.2 [27] and 2.3 [28] each calculate the lattice parameter depending on the molybdenum content in at.-%:

\[
a[\text{Å}] = b[\text{Å}] = c[\text{Å}] = (3.4878 - 0.00340 \cdot x[\text{Mo in at.-%}])[\text{Å}]
\]  

(2.1)
Isothermal Transformation Kinetics in Uranium Molybdenum Alloys

2. Phase Behaviour of Uranium and Uranium Alloys

\[ a[Å] = b[Å] = c[Å] = (3.4808 - 0.00314 \cdot x[\text{Mo in at.-%}])[Å] \]  
(2.2)

\[ a[Å] = b[Å] = c[Å] = (3.4810 - 0.00333 \cdot x[\text{Mo in at.-%}])[Å] \]  
(2.3)

Comparison of these calculations deliver a mean value of

\[ a = b = c = (3.428 \pm 0.005) \text{ Å} \]

for U8wt.-%Mo with a standard deviation of ±1.5%. Increasing the molybdenum content leads to smaller lattice parameters, while decreasing it leads to bigger parameters.

2.4 Thermal Expansion Coefficient

The change in size of materials due to a temperature change is expressed by the coefficient of thermal expansion. Since the thermal expansion is specific for each material, this coefficient is a material constant. The thermal expansion coefficient \( \alpha_L \) is a constant of proportionality between the change in temperature \( dT \) and the relative change in length \( \frac{dL}{L} \) of a solid and therefore is defined as [29]:

\[ \alpha_L = \frac{1}{L} \frac{dL}{dT} \]  
(2.4)

Since the length is temperature dependent, the solution for Equation 2.4 is

\[ L(T) = L(T_0) \cdot \exp \left( \int_{T_0}^{T} \alpha(T) \, dT \right). \]  
(2.5)

Suppose a temperature independent thermal expansion coefficient \( \alpha(T) = \alpha(T_0) \) and an even heating and cooling, respectively, of \( \Delta T = T - T_0 \). Together with the initial length \( L_0 = L(T) \) Equation 2.5 becomes:

\[ L = L_0 \exp(\alpha \cdot \Delta T) \]  
(2.6)

\[ \approx L_0 \cdot (1 + \alpha \cdot \Delta T) \]  
first order approximation of the Taylor series  
(2.7)

Since the thermal expansion is temperature dependent, the coefficient is only representative for a certain temperature or certain temperature intervals.
CHAPTER 3

Isothermal Transformation Kinetics

The transformation of metastable high temperature phases as a function of temperature and time can be described by isothermal transformation diagrams, also known as time temperature transformation (TTT) diagrams. Since phase diagrams, as like Figure 2.5, deliver no information on the kinetics of phase transformation, TTT-diagrams are required to determine the transformation from metastable phases to equilibrium micro structures. Such a diagram shows the decomposition of the high temperature phase over the time for constant temperatures, i.e. time relationships for the phases during isothermal transformation. Therefore, the sections in this chapter will give an introduction to the theory of phase transformation in metals and alloys. It will deal with isothermal transformation kinetics and the Avrami equation as a description of these as well as with time temperature transformation diagrams. Moreover, the kinetics in the $\gamma$-UMo phase decomposition will be introduced.

3.1 Isothermal Transformation Curves and the Avrami Equation

This section will give only an introduction to the theory of isothermal transformation without going too much into detail of the mechanisms of transformation. More detailed information on these theories, as the concept of nucleation rate and phase growth, can be found in *The Theory of Transformation in Metals and Alloys* by Christian [30, 31].

Despite for homogeneous transformations, the transformation process for nucleation and growth reactions is more complex. Where in the homogeneous case, the transformations begins with a linear-like growth, in the latter case a new region is transformed at the time $t = \tau$, where $\tau$ is the induction period for nucleation of the region. After the induction period, the size of the new formed region grows continuously. In most cases, especially when the transformation product and the original phase have the same composition, the transformed amount of material is a linear function of time. The reduction of the growth rate by approaching the end of the transformation can be explained by mutual impingement of forming regions which interfere with each other’s growth. The fraction volume of transformed regions as a function of time, i.e. a growth curve, increases slowly at the beginning, then more rapidly and slows down again in the end and, therefore, delivers a sigmoidal shape shown schematically in Figure 3.1a. The induction period $\tau$ is obtained by definition by the intercept of the time axis with the extrapolated linear portion of the curve. Moreover, the intercept of this linear part with the saturation gives the end
3.2. Isothermal Transformation Curves and the Avrami Equation

(a) Growth curve for a product region with the induction period $\tau$ [30]

(b) TTT-diagram (top) and growth curve (down) for two transformations at different temperatures [35]

**Figure 3.1:** Comparison between a growth curve and a corresponding TTT-diagram - (a) shows a schematic growth curve; (b) shows the growth curve for different temperatures and how these curves determine the TTT-diagram

To describe the nucleation and growth reactions, and therefore the shape of the growth curve, Avrami proposed the use of the following general solution for three-dimensional nucleation and growth process:

$$\xi = 1 - \exp(-kt^n)$$  \hspace{1cm} Avrami Equation \hspace{1cm} (3.1)

with $n = 3$ for zero nucleation rate, $3 < n < 4$ for a decreasing nucleation rate, $n = 4$ for a constant nucleation rate and $n > 4$ for an increasing nucleation rate [31], the rate constant $k$, time $t$ and the transformed fraction $\xi$. Thereby, the rate constant $k$ contains the nucleation rate and the growth rate. Equation 3.1 can only be applied in practice when some assumptions are made for the nucleation as well as the growth rate. The assumptions made by Avrami’s theory are that the nucleation is either constant or else maximum at the beginning and decreases during the transformation. Moreover, the growth rate is assumed to be isotropic. More detailed derivations are found in *The Theory of Transformation in Metals and Alloys - Chapter 1.4* by Christian [30, 31] and in *Kinetics of Phase Change. I-III* [32–34] by Avrami.
3. Isothermal Transformation Kinetics

Figure 3.2: Eutectoidal transformation of a high temperature γ-phase into two phases α and β - (a) shows the equilibrium diagram of an alloy; (b) shows the TTT-diagram for one composition of this alloy

3.2 Isothermal Transformation Diagrams

A complete isothermal transformation diagram can be obtained by plotting the fraction of a phase transformation, introduced in Section 3.1, as a function of time and temperature. Figure 3.1b shows the determination of an isothermal transformation diagram out of growth curves of an individual phase at different temperatures. [35]

Isothermal transformation diagrams, also denoted as time-temperature-transformation (TTT) diagrams, give several information like the nature of the transformation, the rate of transformation, the stability of phases under isothermal conditions or the temperature or time required to start or finish a transformation. Thereby, they describe transformation only for alloys which have been quenched from the high temperature phase to a designated temperature and kept at this temperature during the transformation process. Since the transformation strongly depends on the composition of the alloy, a TTT-diagram is only valid for an individual composition. Decompositions of the high temperature phase into other phases are also known as eutectoidal reactions, since the transformation will begin at temperatures below the eutectoid temperature. The eutectoidal transformation from a high temperature γ-phase into two phases α and β is shown in Figures 3.2a and 3.2b. Above the eutectoid temperature only the proeutectoid α-phase is formed, where below the eutectoidal reaction takes place. In the upper region, in Figure 3.2b above T₁, only the high temperature γ-phase is present. [31]

The typical curves in a TTT-diagram are C-shaped and therefore known as C-curves. For material which has been cooled continuously to lower temperature, continuous cooling transformation (CCT) diagrams are required. The latter show the extent of transformation depending on time for a continuous cooling process. [36]
3.3 Phase Decomposition of the High Temperature $\gamma$-Phase in U8wt.-%Mo

Since this thesis deals with the isothermal transformation in U8wt.-%Mo, this section presents the phase decomposition of this alloy in more detail. Noteworthy is that in the case of uranium-molybdenum alloys with a high solute, there is no difference between the reactions that occur after quenching to the designated reaction temperature and those that occur in alloys previously quenched to room temperature and then heated to the reaction temperature [22]. This makes it possible to prepare samples in advance of an experiment and store them for any time period.

The metastable high temperature phase in uranium-molybdenum is the body-centered cubic $\gamma$-UMo phase. Via several transformation processes the $\gamma$-UMo decomposes into the thermal equilibrium micro structure, which is a mixture of the orthorhombic $\alpha$-U and tetragonal $\gamma'$-phase, i.e. the intermetallic compound $U_2Mo$. Assuming that the equilibrium micro structure consists of pure $\alpha$-U and $U_2Mo$, calculating the composition of the U8wt.-%Mo alloy would result in an $\alpha$-U content of about 52% and an $U_2Mo$ content of about 48%. This describes the equilibrium structure not exactly, since during the decomposition, the result is an $\alpha$-phase enriched with molybdenum rather than pure $\alpha$-U [37]. Moreover, the molybdenum content in $U_2Mo$ is not necessarily exactly 33wt.-%.

Figure 3.3 shows the isothermal transformation diagram of U8wt.-%Mo for temperatures between 300°C and the upper critical temperature at 587°C. Thereby, the diagram was not obtained by collecting growth curves at different temperatures as shown in Figure 3.1b. The approach was annealing samples for different durations at different temperatures and examine them via metallurgical methods. The exact definition for the start of phase decomposition was not given. If there was a change in the structure, it was supposed that the material already experienced the start of phase decomposition.

Above the upper critical temperature, only the $\gamma$-phase is present, whereas for below, the decomposition of the $\gamma$-phase is relatively complex and driven by several mechanisms. In accordance with Repas et al. [38] and Blake et al. [22], the mechanisms will be divided into high-, intermediate- and low-temperature reactions.

The high-temperature reactions are regarded for temperatures above 450°C. The subcritical decompositions are initiated by a cellular reaction. Against the expectations for normal eutectoid reactions, the $\gamma'$-phase is not precipitated initially but originates during the cellular reaction by isothermal treatment. This means that the decomposition starts with $\alpha$-U and enriched $\gamma$-UMo rather than with $\alpha$-U and $U_2Mo$. Besides the cellular reaction, the precipitation of $\alpha$-U in a Wiedmannstätten form is another mechanism present in the high-temperature regime. Thereby, the precipitation of $\alpha$-U happens not at grain boundaries but inside the grains itself. The extent of this process depends on the molybdenum content and increases significantly for decreasing the transformation temperature [38]. The cellular reaction transforms the entire $\gamma$-phase even in the region between the eutectoid temperature of 574°C and the upper critical temperature. Hence, this region contains $\alpha$-U and enriched $\gamma$-UMo and the curve for complete transformation in Figure 3.3 approaches the upper critical temperature asymptotically.

Below 375°C, low-temperature decomposition is present which is initiated by formation of ordered $U_2Mo$. The $U_2Mo$ is the initial product and formed without the presence of $\alpha$-U, whereas
the latter is precipitated subsequently. This means that the Mo content in the γ-UMo is depleted successively. Contrary to cellular transformation, the products in low-temperature processes exhibit a discrete lattice relationship between the initial and the transformed phases. Since such coherent precipitates generally retrogress and reverse to their origin by raising the temperature, Repas et al. heated samples which have been isothermally transformed at 300 °C and 350 °C for 2 minutes at 500 °C. As a result, the phases retrogress and reverse to their origin phase.

In the intermediate-temperature regime between 375 °C and 450 °C the decomposition consists of both reactions, the high- and low-temperature. The transformation is initiated by the cellular reaction but is arrested as the matrix transformed due to the low-temperature mechanism as well as the formation of Widmannstätten α-structure. [22, 38, 39]
This chapter introduces the theory of the crystallographic phase analysis performed to investigate the crystal structure. Moreover, explanatory annotations for the understanding of the Rietveld refinement results are treated.

4.1 Crystallographic Phase Analysis

The crystal structure, and therefore the phases present inside the specimens after heat treatment, can be examined via diffraction measurements, i.e. X-ray and neutron diffraction. Although the physical processes of neutron and X-ray scattering are different, the resulting diffraction patterns are analysed the same way. Diffraction occurs when the electromagnetic radiation or the neutron particle wave, respectively, incident on the crystal structure and undergo constructive interference according to Bragg’s law shown in Figure 4.1. Therefore, the incoming wavelength has to be in the range of the atomic spacings inside the crystals. Depending on the lattice constants $d_{hkl}$ in the crystallite, constructive interference occurs at certain angles according to Bragg’s law

$$2d \sin \theta_B = n\lambda$$ (4.1)

with the Bragg angle $\theta_B$, the wavelength of the incident beam $\lambda$ and $n$ being an integer.

The randomly distributed crystallites in polycrystalline material have their lattice planes in every possible orientation to the beam, as it would be for powder samples. Therefore, Bragg peaks are found at the Bragg angles corresponding to all different lattice constants in the specimens. As a result the peaks’ position delivers the lattice constants and their relative intensity represents the amount of the particular phase as well as the type of atoms present in this phase. For measuring powder diffraction, two geometries are used, depending on the type of scattering being present. Bragg reflections at the surface of the sample, as it is the case for XRD, uses the Bragg-Brentano-Geometry shown in Figure 4.2a whereas for transmission the Debye-Scherrer-Geometry depicted in Figure 4.2b is required. The latter geometry is present for measurements with high energy X-rays and neutrons.
4.1. Crystallographic Phase Analysis

The connection between the peak position, i.e. Bragg-angle $\theta_{hkl}$, and the lattice parameters of the crystal structure can be seen in Bragg’s law. Equation 4.1 gets

$$\lambda = 2d_{hkl} \sin \theta_{hkl} \quad(4.2)$$

$$\Leftrightarrow \quad \theta_{hkl} = \arcsin \left( \frac{\lambda}{2d_{hkl}} \right) \quad(4.3)$$

$$\Leftrightarrow \quad d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \quad(4.4)$$

with the Miller indices $hkl$.

The lattice spacing $d_{hkl}$ can be calculated, depending on the lattice system of the crystal:

Cubic:

$$d_{hkl}^{-2} = \frac{h^2 + k^2 + l^2}{a^2} \quad(4.5)$$

Tetragonal:

$$d_{hkl}^{-2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad(4.6)$$

Orthorhombic:

$$d_{hkl}^{-2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad(4.7)$$

Hexagonal:

$$d_{hkl}^{-2} = \frac{4 (h + k)^2}{3 a^2} + \frac{l^2}{c^2} \quad(4.8)$$

Monoclinic:

$$d_{hkl}^{-2} = \frac{1}{\sin^2 \beta} \left[ \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \left(2hl \cos \left( \frac{\beta}{ac} \right) \right) \right] \quad(4.9)$$
4. Analysing and Evaluation Methods

(a) Bragg-Brentano-Geometry: Bragg reflections in the first atom layers of the sample

(b) Debye-Scherrer-Geometry: Bragg reflections inside the sample during the transmission of the incident beam

Figure 4.2: Geometries used for powder diffraction
4.2. Rietveld Refinement

In 1969 Rietveld introduced a refinement method for nuclear and magnetic structures which allows the quantitative phase analysis of the crystallographic structure of powder samples [40]. The Rietveld Refinement Method uses a least-squares refinement on a theoretical profile until it matches the measured data. Thereby, not only positions, intensities and shapes of the individual peaks but also background and instrumental parameters are considered. For the Rietveld refinement of the diffraction patterns in this work, the FullProf Suite software package has been used [41, 42].

As already mentioned, Rietveld refinement method delivers quantitative information on the crystallographic structure. According to Equations 4.5-4.9, the calculated peak positions define the lattice parameter along with the crystal structure. Beside the structure, also the phase composition, and hence the chemical composition, inside the specimen is calculated.

The obtained scale factors correspond to the phase contribution to the whole pattern and, therefore, can be used to calculate the weight fraction of the single phases. In Equation 4.10 the refined scale factors are used to determine the weight fraction of each crystallographic phase:

\[
W_j = \frac{S_j Z_j M_j V_j / t_j}{\sum_i (S_i Z_i M_i V_i / t_i)}
\]  
(4.10)

where \( S_j \) is the scale factor, \( Z_j \) the number of formula units per unit cell, \( M_j \) the mass of the formula unit, \( V_j \) the unit cell volume and \( t_j \) the Brindley particle absorption contrast factor for phase \( j \) [42].

By discussing the refined result it is necessary to assess the quality of the fit. This can be done by regarding the Rietveld discrepancy values. Therefore, it is essential to know how these values are interpreted. In 2006, Toby [43] discussed the goodness-of-fit and how to interpret the various Rietveld discrepancy values. The Rietveld refinement method adjusts the fit insofar that the difference between the observed data and the calculated fit becomes minimal. The first discrepancy value is the profile R-factor:

\[
R_p = \frac{\sum_i |y_{C,i} - y_{O,i}|}{\sum_i y_{O,i}}
\]  
(4.11)

from which the weighted profile R-factor is defined as

\[
R_{wp}^2 = \frac{\sum_i w_i (y_{C,i} - y_{O,i})^2}{\sum_i w_i (y_{O,i})^2}
\]  
(4.12)

where \( y_{C,i} \) and \( y_{O,i} \) are the calculated and observed intensities, respectively, and \( w_i = (\sigma^2 [y_{O,i}])^{-1} \) is the weight. Hence, the weighted profile R-factor describes the square root of the minimized difference between the calculated and observed data, scaled by the weighted intensities. If the model exactly predicts the observed data, the expected value for \( w_i (y_{C,i} - y_{O,i})^2 \) is 1, the best possible \( R_{wp} \) is achieved and called expected R-factor:

\[
R_{exp}^2 = \frac{N}{\sum_i w_i (y_{O,i})^2}
\]  
(4.13)
where $N$ is the number of data points. The $\chi^2$ for the fit can be determined as follows:

$$\chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2$$  \hspace{1cm} (4.14)

and is in literature often denoted as $G^2$, where $G$ is called the *goodness-of-fit*.

To conclude, these discrepancy values not only assess the structural model but also the background, peak positions and peak shapes. This also explains the differences between refinement performed on neutron diffraction data and high energy X-ray diffraction data, respectively. The higher signal to noise ratio of X-ray data on the one hand decreases $R_{exp}$, but on the other increases the difference between $R_{exp}$ and $R_{wp}$ and hence make $\chi^2$ worse, even with a good fit. Moreover, minor imperfections like the parasitic scattering at the aperture, as reported for high energy X-ray studies in Chapter 6.2.2, lead to big $\chi^2$ and $R_{wp}$ values. It should be noted particularly that higher-quality datasets can show worse $\chi^2$ and $R_{wp}$ values compared to lower-quality datasets, without showing a lack of quality in the calculated model. Therefore, not only the discrepancy values should be considered but also the graphical result for the calculated model and its difference to the observed pattern needs to be taken into account for a qualitative assessment of a Rietveld refinement.
Part II

Experiment
CHAPTER 5

Sample Preparation

For the detailed study of the $\gamma$-phase decomposition in U8wt.-%Mo, in total 26 monolithic samples with depleted uranium (0.22at.-%$^{235}$U) have been prepared according to Table 5.1. All these samples originate from an ingot provided by AREVA-CERCA. A chemical analysis on five of the 20 bricks along this ingot was performed by AREVA-CERCA, which is attached in Appendix A.

For the different examination methods, a certain geometry of the samples was required. X-Ray diffraction studies required thin slices, microscopic measurements even demanded polished slices. For experiments with neutrons, bulk samples are sufficient and therefore further processing of the specimens was not required. The following sections in this chapter give a detailed insight into the sample preparation processes performed throughout this thesis. All preparation was performed in a radionuclide laboratory at the FRM II and therefore in a controlled area.

5.1 Cast Samples

Pieces with a mass of about 4g were cut down from the U8wt.-%Mo ingot. The pieces were melted with an Electric Arc Furnace (EAF, Figure 5.1a) from Edmund Bühler GmbH (Mini Arc Melting System MAM-1D-H180). The arc melting includes several steps to reduce the amount of oxygen inside the furnace' atmosphere. These steps were initiated in order to keep the pollution inside the samples as small as possible. The first step was evacuating the furnace followed by inverting its atmosphere with argon. Another precaution was melting a zirconium-titanium alloy right before melting uranium. Thereby, zirconium acts as an oxygen getter. For homogenization of the alloys, the samples were turned over and melted for three times. Between each step the furnace was evacuated and flooded with fresh argon for a cleaner atmosphere. The last step was casting the uranium into a water cooled copper mould with a cylindrical shape with a diameter of 6 mm. Thereby, the molten material solidifies instantly when the power supply of the arc melter is cut off. The samples then have a length between 10-20 mm and a diameter of 6 mm.
### 5.1. Cast Samples

**Table 5.1:** List of U8wt.-%Mo samples with information on heat treatment, i.e. homogenization and annealing temperatures and duration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>Homogenization</th>
<th>Isothermal Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Duration [h]</td>
<td>Temp. [°C]</td>
</tr>
<tr>
<td>A-1</td>
<td>A-initial</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-2</td>
<td>A-initial2</td>
<td>as cast</td>
<td>as cast</td>
</tr>
<tr>
<td>A-3</td>
<td>A-425C24h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-4</td>
<td>A-400C48h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-5</td>
<td>A-450C3h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-6</td>
<td>A-475C3h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-7</td>
<td>A-450C6h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-8</td>
<td>A-475C16h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-9</td>
<td>A-500C6h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-10</td>
<td>A-450C24h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-11</td>
<td>A-450C16h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-12</td>
<td>A-500C16h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-13</td>
<td>A-450C48h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-14</td>
<td>A-500C3h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-15</td>
<td>A-400C24h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-16</td>
<td>A-475C6h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-17</td>
<td>A-500C48h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-18</td>
<td>A-425C6h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-19</td>
<td>A-475C48h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-20</td>
<td>A-425C3h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-21</td>
<td>A-475C24h</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-22</td>
<td>A-450Cinsitu</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-23</td>
<td>A-475Cinsitu</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-24</td>
<td>A-500Cinsitu</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-25</td>
<td>A-525Cinsitu</td>
<td>48</td>
<td>900</td>
</tr>
<tr>
<td>A-26</td>
<td>A-425Cinsitu</td>
<td>48</td>
<td>900</td>
</tr>
</tbody>
</table>
5. Sample Preparation

(a) Electric arc furnace

(b) Diamond wire saw

(c) High temperature furnace in the radionuclide laboratory

Figure 5.1: Sample preparation equipment in the radionuclide laboratory
5.3. Heat Treatment

5.2 Heat Treatment

5.2.1 Homogenization

After casting, the samples were homogenized at 900 °C for 48 h. Both, the homogenization as well as the annealing were performed in a high temperature furnace under vacuum shown in Figure 5.1c. The furnace is the tube furnace Heraeus ROF where temperatures up to 1300 °C are achievable.

5.2.2 Isothermal Temperature Treatment

For temperature treatment, the uranium samples were wrapped inside zirconium foil. Thereby, the zirconium again serves as an oxygen getter. Before evacuating, the tube was inert with argon to minimize the remaining amount of oxygen. Moreover, before heating the uranium samples only zirconium in the very front of the tube was heated. This was another step to reduce remaining oxygen and hence prevent the samples from oxidation. After these precautions, the samples itself were put in the center of the furnace. The temperature was verified with a K-type thermocouple in contact with the sample and therefore reliable information on temperature was guaranteed. Since the temperature input at the furnace was about 25 °C above the actual temperature at the sample, the temperature had to be readjusted during the first heat treatments.

Samples with temperatures between 400 °C and 550 °C in steps of 25 °C were prepared. The annealing durations were 3 h, 6 h, 16 h, 24 h, 48 h, respectively. Table 5.1 and Figure 5.2 summarise the different samples prepared for the experiments.

![Figure 5.2: TTT-diagram for an U8wt.-%Mo alloy [38] where all measured samples are listed; i) blue rectangle: neutron diffraction; ii) blue circle: high-energy X-ray diffraction; iii) red arrow: neutron diffraction during in-situ annealing](image-url)
5.3 Surface Preparation

For evaluation of the samples and first experiments thin, polished slices were required. Therefore slices with a thickness of about 1 mm and a diameter of 6 mm were cut down from the cast ingots with a Well Diamond Wire Saw Type 3242-3 shown in Figure 5.1b. A diamond wire with a diameter of 0.22 mm together with a low feed rate and high speed rotation was chosen in order to ensure best cutting edges. The wire was cooled by an emulsion dissolved in water. Besides cooling the emulsion acts as a lubricant and ensures a longer life of the diamond wire.

For promising measurements, as little as possible scratches and impurities should be on the surface of the samples. To achieve this, the surface was treated by various methods of grinding, polishing and etching. Therefore, the samples were embedded in Struers Specifix and ground, first with coarse then with fine sand paper. The mechanical polish was finished with a 1 µm diamond paste. The specimens were then attack-polished in a mixture of 4.75 % hydrogen peroxide and 95.25 % Struers OP-S Suspension. Grinding and polishing was performed with the ATM SAPHIR 520/530. The single steps in more detail were:

Grinding:

- coarse grinding with P240 grit, 20 N for 30 s
- fine grinding with P600 grit, 20 N for 30 s
- very fine grinding with P1200 grit, 20 N for 30 s

Polishing:

- 9 µm polishing with a Struers MD-Largo polishing cloth and Struers DiaPro Allegro/Largo 9 µm suspension, 15 N for 60 s
- 3 µm polishing with a Struers MD/DP-Dac polishing cloth and Struers DiaPro Dac 3 µm suspension, 15 N for 60 s
- 1 µm polishing with a Struers MD/DP-Nap polishing cloth and Struers DiaPro Nap-B-1 1 µm suspension, 15 N for 60 s
- attack polishing with a Struers MD/OP-Chem polishing cloth and a mixture of 95.25 % Struers OP-S suspension and 4.75 % hydrogen peroxide, 10 N for 180 s

In Figure 5.3a three stages of sample preparation are shown, i.e. cast ingot, slice and embedded/polished slice. The Figures 5.3b and 5.3c show the sample surface before and after polishing, respectively. The deep scratches created by cutting the samples seen in Figure 5.3b are gone after polishing and only fine scratches are left as can be seen in Figure 5.3c.
5.3. Surface Preparation

(a) Stages of sample preparation: A - cast ingot; B - slice; C - embedded slice

(b) Surface after cutting

(c) Surface after 1 µm polishing step

Figure 5.3: Sample preparation and polishing; (b) and (c) show optical microscope images of the surface before and after polishing
CHAPTER 6

Examination Methods

For the examination of the specimens, various methods were used. For an initial assessment of the crystal structure, **X-ray Diffraction (XRD)** was performed. Moreover, the microscopic structure was examined with **Optical Microscopy (OM)** and **Scanning Electron Microscopy (SEM)**. **Energy Dispersive X-ray Spectroscopy (EDX)** within the SEM was used to examine the pollution with other elements inside the UMo samples. The key measurements to determine the crystal structure as well as the phase composition inside the samples were performed with high-energy X-rays, at the **High Energy Materials Science Beamline (HEMS)** at the **Deutsches Elektronen Synchrotron (DESY)**, and with powder diffraction with neutrons, at the **High Resolution Powder Diffractometer (SPODI)** at the FRM II. For quantitative information on phase decomposition, in-situ annealing measurements at the **Materials Science Diffractometer (STRESS-SPEC)** at the FRM II were realized. The following sections give a brief insight into these examination methods.

### 6.1 Microscopic Structure Examination and Chemical Composition

In order to evaluate the pollution of the samples with other materials, some specimens were examined via metallurgical methods. Figures 6.1a and 6.1b show images obtained via optical microscopy and scanning electron microscopy, respectively.

**Figure 6.1:** Microscope images of sample A-425C6h

(a) Optical microscope image

(b) Scanning electron microscope image; marked areas were examined with EDX
6.2. Crystallographic Phase Analysis

and scanning electron microscopy, respectively. On both images the same structure is observable, which is due to the slight decomposition after 6h of annealing at 425°C. The SEM image shows, despite the OM image, black areas as the one labelled with 3 in Figure 6.1b. The darker area 1, the brighter area 2 and the spot 3 were analysed with energy dispersive X-ray Spectroscopy. The result shows that the areas 1 and 2 have a slightly different molybdenum content. Moreover, the regions are polluted with some carbide and oxides. The inclusions in the zone boundaries are enriched in carbides, oxides and nitrides. Further surface investigations with EDX showed randomly distributed inclusions with a high concentration of molybdenum and some vanadium. Further measurements with neutrons and X-rays, respectively, are not influenced by these inclusions since their percentage of the whole sample is negligible.

Since already first microscopical investigations revealed interesting results, a bachelor thesis was conducted [44]. This work dealt with the preparation process and metallurgical investigation of UMo.

6.2 Crystallographic Phase Analysis

6.2.1 X-Ray Diffraction

The XRD measurements were performed at the crystallography section of the Fakultät für Geowissenschaften - Department für Geo- und Umweltwissenschaften at the Ludwigs-Maximilians-Universität in Munich. The X-ray beam has an energy of the copper $K_α$-line of $E_{K_α} = 8.048$ keV what defines the wavelength $λ_{K_α} = 1.5406$ Å. To avoid preferred orientation of the Bragg reflections due to grain structures on the sample surface, the sample holder – and therefore the sample – was rotated during the measurements. Moreover, since an uneven sample surface leads to a shift of the reflected peaks the sample needs to be planar. To avoid contamination from uranium at the experiment, the samples were sealed in kapton foil. This is a commonly used material for windows and sample containers at X-ray sources due to its high transmittance to X-rays. Moreover, kapton only adds an underground to the diffraction pattern and hence has no strong impact on the results of the measurements. The X-ray beam hits the sample surface under the incident angle $θ$ while the detector is located at the angle $2θ$. During this so called $θ/2θ$-scan, Bragg reflections are detected when $θ = θ_B$.

6.2.2 High-Energy X-Ray Diffraction

The HE-XRD measurements were done at the Positron-Electron Tandem Ring Accelerator III (PETRA III) at the DESY in Hamburg. The High Energy Materials Science Beamline (HEMS) has a main energy of 100 keV and is tunable in the range of 35-200 keV [45].

With an energy of $E = 100$ keV the wavelength is calculated by Equation 6.1, where $h$ is the planck constant and $c_0$ the speed of light, to $λ = 0.124$ Å.

$$λ = \frac{hc_0}{E}$$

To verify the wavelength, the NIST LaB$_6$-660a standard was measured and Rietveld Refinement was performed what confirmed the wavelength and hence the energy.
In contrast to lower energy XRD, the incident beam penetrates the sample and therefore underlies the transmission geometry according to Debye-Scherrer. The decline in intensity of the incident X-ray beam inside an absorbing material is calculated by the Lambert-Beer law

\[ I = I_0 \exp \left( -\frac{\mu}{\rho} x \right) \] (6.2)

with the mass thickness \( x = \rho d \), the materials thickness \( d \), the attenuation coefficient \( \mu \) and the materials density \( \rho \), whereas the mass attenuation coefficient is defined as \( \frac{\mu}{\rho} \). For a solution or an alloy, the actual attenuation coefficient is calculated by

\[ \mu = \sum_i \left( \frac{\mu_i}{\rho_i} \right) \rho_i \] (6.3)

With the X-ray mass attenuation coefficients for \( E_{X-ray} = 100\text{keV} \) [46]

uranium: \( \left( \frac{\mu}{\rho} \right)_U = 1.954 \text{ cm}^2 \text{ g}^{-1} \)

molybdenum: \( \left( \frac{\mu}{\rho} \right)_Mo = 1.096 \text{ cm}^2 \text{ g}^{-1} \)

and the density for U8wt.-%Mo of \( \rho_{U8Mo} = 17.282 \text{ cm}^2 \text{ g}^{-1} \) [47], the penetration depth \( L_p \), i.e. decrease of the intensity to \( \frac{1}{e} \approx 37\% \), and the skin depth \( L_e \), i.e. decrease of the intensity to \( \frac{1}{e^2} \approx 13\% \) are

\[ L_p = 307 \mu m \]

\[ L_e = 614 \mu m \]

Due to these results and for a high intensity after the transmission, the samples were manufactured to have a thickness of approximately 150 \( \mu m \). The remaining intensity after transmission is calculated by Equation 6.2 to 61\% of the initial intensity. This is a good compromise between the amount of scattered particles and a high intensity after penetration.

It should also be mentioned that there is a parasitic scattering effect due to the aperture system in the experiment. This causes small peaks at 0.21Å\(^{-1}\) in the diffraction patterns obtained at HEMS. Figure 6.2a shows the detector image of a measurement at the high-energy X-ray beamline, where the parasitic scattering effect is highlighted. The impact on the diffraction pattern is shown in Figure 6.2b, where the magnified region shows the two peaks caused by the aperture.

6.2.3 Neutron Diffraction (SPODI)

The High-Resolution Structure Powder Diffractometer SPODI at the FRM II is well suited for studies of the crystal structure of powder samples with thermal neutrons. With a very high monochromator take-off angle of 155\(^{\circ}\) and a large monochromator-to-sample distance of 5 m, the instrument has a high resolution and a good profile shape [48]. In total 80 detector tubes cover an angle of 160\(^{\circ}\). In Figure 6.3, the experimental set-up and the detector arrays are shown. Since every detector covers 2\(^{\circ}\), the multidetector array requires a stepwise positioning to collect a full diffraction pattern with a desired angular resolution. Measurements were performed, depending on the samples, with a resolution of 0.1\(^{\circ}\) and 0.05\(^{\circ}\) and therefore 20 and 40 steps were required, respectively. Such a moving multidetector concept results in a good resolution over a broad
6.2. Crystallographic Phase Analysis

(a) Detector image of the measurement; parasitic scattering effect is highlighted in red

(b) Rietveld refinement with enlarged detail which shows the two peaks caused by the aperture; the effect is not considered in the fit

Figure 6.2: Parasitic scattering effect due to the aperture system at the HEMS on the example of sample A-475C16h; (a) shows the detector image; (b) shows the Rietveld refinement of the diffraction pattern

scattering angle regime from 0-160°.

For the experiment, a germanium monochromator Ge(551) was chosen which lead, together with the take-off angle of 155° and a 5 m distance to the sample, to a wavelength of $\lambda = 1.549$ Å. The measurement of the NIST Si-640c standard verified the wavelength close to this value. A Rietveld refinement of the diffractogram seen in Figure 6.4a determined the wavelength to $\lambda = 1.548$ Å.

Since the intensity is proportional to the particle number for scattering, the samples should be in the size of the beam spot for maximum yield. For safety reasons and to avoid a contamination at the experiment, the bulk samples have been sealed inside vanadium tubes before the measurements. Moreover, due to a noticeable grain structure inside the sample, it was necessary to rotate the vanadium tubes during the measurements.

The instrumental set-up allows to install six samples at once. The samples can be moved automatically in the beam and, moreover, can be rotated during measurements. In a first step, short-time measurements for 15 min of all samples gave information on the positioning, the required resolution as well as on the scan time for each individual measurement. The six measurements can be programmed and are then performed automatically. Resolutions between 0.05° and 0.1° along with scan times between 6 h and 8 h were chosen depending on the phases present in the individual samples.

Due to the geometry of the experimental set-up, the detector image obtained at SPODI needs to be corrected to achieve the true diffraction pattern. Figure 6.5 shows the collected detector image together with two correction steps. The uncorrected image shows the intersection of the
6. Examination Methods

Figure 6.3: Experimental set-up at Spodi

(a) Schematic representation of Spodi [1]
(b) Set-up of Spodi at the FRM II

Figure 6.4: Rietveld refinements of the NIST Si-640c standards at Spodi (a) and Stress-Spec (b), respectively
6.3 In-Situ Annealing Measurements

Observing the phases present in the samples during the annealing process gives information on the transformation kinetics. Hence, in-situ annealing measurements were performed. Hereby, the focus was not on the phase analysis and the amount of each phase inside the compound. The experiment aimed, in particular, at the start of phase decomposition along with the growth of phases during annealing. Moreover, since measurements were performed also during the heating and cooling processes, respectively, the peak positions as a function of temperature could be observed. In a final step, the transition into the high temperature phase was observed.

6.3.1 Neutron Diffraction (Stress-Spec)

The experiment was performed at the Materials Science Diffractometer Stress-Spec which is located in the experimental hall of the FRM II and uses thermal neutrons. A range of three different monochromators and a take-off angle variable from 35-110° allow wavelength adjustments [49]. By analysing the Rietveld refinement of the diffractogram of the measured NIST Si-640c standard shown in Figure 6.4b, a wavelength of $\lambda = 1.914\,\text{Å}$ was determined. Due to an inhomogeneous detector it is necessary to correct measured diffraction patterns before analysing them. Therefore, an empty vanadium container inside the experimental set-up was measured and the resulting diffraction pattern was used as a dark image, i.e. the correction data was subtracted from the collected diffraction patterns. The detector image used for correction is shown in Figure 6.6a and an exemplary detector image of an UMo sample after 7 h annealing at 450°C is shown in Figure 6.6b.
The annealing was performed in a high temperature furnace under vacuum. Hereby, one of the advantages of neutron measurements is at hand. Since the experimental set-up is easily penetrated by neutrons, measurements of samples are possible, which are located inside complex set-ups. In Figure 6.7a, the high temperature vacuum furnace installed at the Stress-Spec beam line is shown.

As for the measurements at SPODI, the samples were sealed inside vanadium tubes. Moreover, these tubes needed to meet some requirements in order to mount them at the specimen carrier seen in Figure 6.7b. Besides that, a special design was required to get the thermoelements close to the sample to get reliable information on temperature. Therefore, the vanadium tube was designed especially for measurements of bulk samples inside high temperature vacuum furnaces.
6.3. In-Situ Annealing Measurements

(a) High temperature vacuum furnace installed at Stress-Spec

(b) Specimen carrier

Figure 6.7: Experimental set-up at Stress-Spec
Part III

Results and Discussion
In this chapter, the results obtained by X-ray and neutron diffraction studies will be presented and discussed. The results of Rietveld refinement on the measurements of heat treated U8wt.%Mo samples will later be compared and complemented with the data obtained during in-situ annealing. The diffraction data collected by neutron diffraction and high-energy X-ray diffraction, respectively, has been analysed with the *FullProf Software* package [41] using Rietveld refinement method [40].

### 7.1 Data Analysis

To analyse the phase decomposition described in Section 3.3, five phases have been included in the refinement process. Thereby, four of them describe the UMo-particles:

γ-UMo-a, γ-UMo-b, α-U (α′-U, α″-U) and U₂Mo

The γ-UMo-a represents the initial γ-phase and γ-UMo-b a molybdenum enriched γ-phase which precipitates during the phase decomposition reactions. Hence, the latter phase has smaller lattice parameters. α-U and U₂Mo are the products of decomposition, whereas the α-phase can also be the distorted states α′-U or α″-U, dependent on the temperature the reaction takes place. Due to the inclusion of oxide and nitrite, one other phase has been added:

UC/UN

Since UC and UN have the same space group, i.e. Im-3m, and very similar lattice parameters, only one phase representing both of them has been included and named UC in every pattern. Figure 7.1 shows an exemplary diffraction pattern of a decomposed U8wt.%Mo sample in the angular range of sin (θ) / λ = 0.185 Å⁻¹ to 0.225 Å⁻¹. Thereby, all phases contributing to the peaks are depicted.

For the refinement, Pseudo-Voigt functions have been chosen to simulate the Bragg peak shapes since the shape can be described best by a convolution of a Gaussian profile and a Lorentzian profile. The Background was described by selected background points and a linear interpolation between these points, rather then by mathematical functions. Besides the scale factors and the lattice parameters, also the peak shape parameters have been refined. Moreover, to improve the quality of the fit, the background points have been refined as well.
7.2 Initial U8wt.-%Mo Phase

The starting point, a highly homogeneous $\gamma$-U8wt.-%Mo alloy, is equal for each isothermal treatment as the manufacturing procedure was the same for all samples. Moreover, this was verified by measurements. Thereby, the homogeneity only refers to the phase composition inside the specimens and not to the present grain structure. A diffractogram of such a specimen was taken once and is used as reference material for the initial state before each decomposition. Figure 7.2a shows the Rietveld refinement of the diffraction pattern collected at SPODI. The uncorrected and corrected detector image is shown in Figure 7.2b. In the following, only the corrected images of measurements at SPODI will be shown.

The results of the refinement process are summarised in Table 7.1. A lattice parameter of $a=b=c=3.427\,\text{Å}$ for the $\gamma$-U8wt.-%Mo is in good agreement with the empiric Formulas 2.1 - 2.3. A refinement with two slightly different $\gamma$-UMo phases was not successful. Accordingly, the sample can be considered to have only one $\gamma$-phase after the heat treatment. In the following, isothermal studies at different temperatures will be discussed.
Figure 7.2: Refinement of the diffraction pattern of the highly homogeneous γ-UMo collected at Spodi - (a) shows the Rietveld refinement result; (b) shows the uncorrected and corrected detector images.
Table 7.1: Lattice constants, crystallographic composition and final agreement factors of the Rietveld refinement of the U8wt.-%Mo reference sample

<table>
<thead>
<tr>
<th>Lattice Constants [Å]</th>
<th>Weight Fraction [wt.-%]</th>
<th>Agreement Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-UMo a=b=c=</td>
<td>3.427</td>
<td>98.93</td>
</tr>
<tr>
<td>UC a=b=c=</td>
<td>4.955</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rwp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rexp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>χ²</td>
</tr>
</tbody>
</table>

7.3 High-Temperature Reactions – 475 °C and 500 °C

For decompositions associated with the high-temperature reaction regime, which has been introduced in Chapter 3, in total nine samples have been prepared. Thereby, five samples were annealed at 475 °C and four samples at 500 °C. The following discussion will begin with the isothermal studies at 475 °C, in order to explain the details on the basis of these results.

7.3.1 Isothermal Studies at 475 °C

Five samples were annealed at 475 °C for either 3h (A-475C3h), 6h (A-475C6h), 16h (A-475C16h), 24h (A-475C24h) or 48h (A-475C48h). Thereby, A-475C3h and A-475C16h were measured with high-energy X-rays, while the other samples were examined with neutrons. As already reported elsewhere, the results for the weight percentages of the single phases obtained by Rietveld refinement can differ slightly between diffraction patterns obtained by X-rays and neutrons, respectively [50].

The diffractograms in Figures 7.3a - 7.5e show the decomposition of pure γ-UMo (Figure 7.2a). For better comparison of the diffraction patterns, the intensity is plotted over \(\sin (θ)/λ\) rather then over \(2θ\) due to the different wavelengths at the respective instruments.

Following discussion is also based on Tables 7.2-7.4, which summarise all data obtained by Rietveld refinement method. Whereby the diffractograms allow only a qualitative comparison of the decomposition, the results obtained by Rietveld refinement give quantitative descriptions of the crystallographic composition in the specimens. The progress of the phase decomposition is discussed with the help of Table 7.2 where the weight fractions of the individual phases are listed. γ-UMo-a is the initial γ-U8wt.-%Mo phase which decomposes according to the high-temperature reactions described in Section 3.3. Besides α-U, another product at the beginning of decomposition during high-temperature reactions is a molybdenum enriched γ-UMo-b. After 3h of annealing, already a great part of the initial γ-UMo is transformed. As expected for high-temperature reactions, the decomposition started with forming α-U and enriched γ-UMo-b. This can be seen by the relatively high content of these two phases. Furthermore, some U₂Mo was already formed.

It should be noted that the two γ-UMo peaks are very close together and therefore distinguishing between these two phases is error-prone. Therefore, it is possible that some content of γ-UMo-a belongs to γ-UMo-b, or vice versa.
Table 7.2: Crystallographic composition of U8wt.-%Mo for isothermal studies at 475 °C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>γ-UMo-a</th>
<th>γ-UMo-b</th>
<th>U₂Mo</th>
<th>α-U</th>
<th>UC</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>54.67</td>
<td>20.32</td>
<td>5.56</td>
<td>18.38</td>
<td>1.07</td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>22.44</td>
<td>27.07</td>
<td>19.42</td>
<td>29.93</td>
<td>1.15</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>16.30</td>
<td>22.02</td>
<td>22.27</td>
<td>38.35</td>
<td>1.06</td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>15.24</td>
<td>5.72</td>
<td>34.78</td>
<td>42.99</td>
<td>1.28</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>13.63</td>
<td>2.61</td>
<td>38.75</td>
<td>44.25</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 7.3: Lattice constants of the phases γ-UMo-a, γ-UMo-b, α-U (α'-U, α''-U) and U₂Mo for the isothermal studies at 475 °C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>γ-UMo-a</th>
<th>γ-UMo-b</th>
<th>U₂Mo</th>
<th>α-U</th>
<th>α-U</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>a=b=c</td>
<td>3.419</td>
<td>3.389</td>
<td>3.400</td>
<td>9.958</td>
<td>2.862</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>a=b=c</td>
<td>3.400</td>
<td>3.362</td>
<td>3.406</td>
<td>9.909</td>
<td>2.862</td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>a=b</td>
<td>3.410</td>
<td>3.373</td>
<td>3.417</td>
<td>9.904</td>
<td>2.867</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>a=b</td>
<td>3.412</td>
<td>3.374</td>
<td>3.419</td>
<td>9.893</td>
<td>2.867</td>
</tr>
</tbody>
</table>

Significant is that the amount of γ-UMo-a drops fast together with a fast growth of α-U. The α-U growth approaches its saturation slowly already before 24h. The amount of γ-UMo-b rises very fast but then decreases fast shortly after reaching its maximum. This can be explained by considering the U₂Mo content which is precipitated during the cellular reaction. The lattice parameters of γ-UMo-b indicate that the enrichment of molybdenum in this phase increases with the time and the phase precipitates U₂Mo at the same time.

Table 7.3 summarises the calculated lattice constants for the two γ-UMo, U₂Mo and α-U phases for each measurement. The behaviour of γ-UMo-b shows the molybdenum enrichment with time. The longer the specimen was annealed, the smaller are the lattice parameter, and hence the higher the molybdenum content is in γ-UMo-b. Thereby, the γ-phases in sample A-475C16h both show a significantly lower lattice parameter. The explanation is that refining two γ-phases was problematic in this sample and therefore also the fit is not as good as for the other measurements. The latter is also expressed by the agreement factors in Table 7.4 where the χ² = 28.3 is much bigger compared to the χ² of the other calculations.

With the calculated lattice parameters for γ-UMo-b, the enrichment of this phase is between 12.3-17.4 wt.-% Mo, neglecting sample A-475C16h. As mentioned in Section 2.3, the γ-phase is stable for a molybdenum content between 4.5-15.5 wt.-% which leads to the assumption that the lattice parameters for the samples A-475C24h and A-475C48h do not represent the true value. An explanation for this is that the main γ-UMo peak and the U₂Mo peak overlap each other. Especially for strongly decomposed specimens, it is hard to determine the exact position of these two peaks and hence the exact lattice parameters. Moreover, the molybdenum content was calculated with empiric Formulas 2.1-2.3, which can be afflicted with an error. The same applies
7.3. High-Temperature Reactions – 475 °C and 500 °C

(a) A-475C3h: 3h at 475 °C; high-energy X-rays

(b) A-475C6h: 6h at 475 °C; neutrons

(c) A-475C16h: 16h at 475 °C; high-energy X-rays

(d) A-475C24h: 24h at 475 °C; neutrons

(e) A-475C48h: 48h at 475 °C; neutrons

Figure 7.3: Rietveld Refinement of the diffraction patterns obtained after 475 °C heat treatment; embedded are the associated 2D patterns obtained by X-ray and neutron diffraction, respectively
Table 7.4: Final agreement factors between calculated and measured data obtained by Rietveld refining the diffraction patterns for the isothermal studies at 475°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Agreement Factors</th>
<th>( R_p )</th>
<th>( R_{wp} )</th>
<th>( R_{exp} )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>6.50</td>
<td>7.66</td>
<td>2.83</td>
<td>7.45</td>
<td></td>
</tr>
<tr>
<td>X-ray</td>
<td>6 h</td>
<td>8.18</td>
<td>7.92</td>
<td>4.39</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>4.78</td>
<td>6.42</td>
<td>1.21</td>
<td>28.3</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>7.47</td>
<td>8.08</td>
<td>3.34</td>
<td>5.92</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>7.48</td>
<td>7.75</td>
<td>4.02</td>
<td>3.77</td>
<td></td>
</tr>
</tbody>
</table>

for the problems with \(\gamma\)-UMo in sample \(A-475C16h\). On closer examination of the diffractograms in Figures 7.3c-7.5e, it becomes clear that the overlapping peaks easily cause difficulties during the refinement of the data.

The calculated lattice parameters for \(\alpha\)-U show expanded parameters \(a\) and \(c\) together with a contracted parameter \(b\) compared to a pure \(\alpha\)-U phase. This indicates that the present uranium phase is the distortion of the \(\alpha\)-phase named \(\alpha'\)-U. The lattice parameters for \(\gamma\)-UMo and \(\alpha\)-U as well as the suggested \(\alpha\)-U-phase are in good agreement with results previously obtained by Palancher et al. in 2012 for U8wt.-%Mo samples [37].

The final agreement factors of the Rietveld refinements, which define the quality of the fit, are shown in Table 7.4. The results are good except for the X-ray pattern taken of sample \(A-475C16h\), as already mentioned above. Another striking aspect is that refinements of X-ray patterns have bigger \(\chi^2\) values, which is explained by one major factor. Although \(R_{exp}\) decreases as the number of counts collected for the diffraction pattern is increased, the difference between \(R_{exp}\) and \(R_{wp}\) becomes larger. Hence, \(\chi^2\) is worse even though the model fitted into the diffraction pattern is improved. The reason for this is that, for diffraction patterns with a very large number of counts, even minor imperfections in the peak shape, peak position and unmodeled features of the background can make it impossible to obtain small values for \(R_{wp}\) and, hence, for \(\chi^2\) [43].

Such an imperfection can be seen in the diffraction patterns collected with HE-XRD, where the scattering at the aperture of the experiment induced small peaks in the diffraction pattern at 0.24 Å\(^{-1}\) which are not included in the fit. Besides the agreement factors, the difference between the data and the calculated pattern – \(Y_{obs} - Y_{calc}\) – can be taken as an indicator for the quality of the fit. This shows that the models obtained for X-ray patterns are not worse than the models obtained for neutron patterns as suggested by the final agreement factors. The discrepancy is well explained by the fact of a much higher number of counts for the measurements with X-rays.

7.3.2 Isothermal Studies at 500°C

Isothermal studies at 500°C were performed on four samples annealed for either 3 h (\(A-500C3h\)), 6 h (\(A-500C6h\)), 16 h (\(A-500C16h\)) or 48 h (\(A-500C48h\)). The specimen \(A-500C3h\) and \(A-500C48h\) were measured with neutrons, specimen \(A-500C6h\) and \(A-500C16h\) with X-rays. The diffractograms in Figures 7.4a - 7.4d will be used for a qualitative comparison of the decomposition, while Tables 7.5-7.7 show the results of Rietveld refinement and therefore provides quantitative information on the crystallographic composition.
Table 7.5 shows the progress of phase decomposition. A similar behaviour compared to the reactions at 475 °C is expected due to the fact that both temperatures belong to the high-temperature reaction regime. However, a noticeable difference can be seen between A-475C3h and A-500C3h. This can be explained with the aforementioned difference between examinations with neutrons and X-rays, respectively. Comparing Figure 7.3a and Figure 7.4a make it obvious that refining neutron diffraction patterns of less strongly decomposed material is pretty difficult. Due to the very sharp peak of the γ-UMo Bragg reflection, small changes to the peak shape parameters cause a huge effect on the crystallographic composition without influencing the quality of the fit in a significant manner. Moreover, it was not possible to refine two different γ-phases inside this diffractogram. Therefore, no quantitative information is given for sample A-500C3h but only the knowledge that decomposition already has started.

Further behaviour of the decomposition can be compared to the isothermal studies at 475 °C. While the γ-phase contents behave the same way, the growth of U₂Mo and α-U is slightly different. The U₂Mo content increases more slowly and, therefore, the α-phase more rapidly. Whereas, the growth of α-U must be treated with caution, since the content of the α-phase in A-500C16h deviates from the results of other phases.

The calculated lattice parameters summarised in Table 7.6 show no distinctive features except for the missing second γ-UMo phase in sample A-500C3h. Again, the distortion of the pure α-U phases suggests the presence of α′-U rather then α-U.

The final agreement factors in Table 7.4 reflect the difficulties with Rietveld refinement of A-500C3h. The high values for χ² for the X-ray examinations have the same reasons as already mentioned above. In these cases, the quality of the fit needs to be evaluated qualitatively by observing the values for Y_{obs}-Y_{calc}, represented by the blue line in the diffractograms.

**Table 7.5:** Crystallographic composition of U8wt.-%Mo for isothermal studies at 500 °C; Composition for sample A-500C3h is excluded, since no reliable quantitative information is given by the refinement

<table>
<thead>
<tr>
<th>Examination Duration</th>
<th>Weight Fraction [wt.-%]</th>
<th>Exami-</th>
<th>Annealing</th>
<th>Weight Fraction [wt.-%]</th>
<th>Exami-</th>
<th>Annealing</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron 3h</td>
<td>γ-UMo-a 22.47</td>
<td>γ-UMo-b 26.92</td>
<td>U₂Mo 13.47</td>
<td>α-U 36.22</td>
<td>UC 0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray 6h</td>
<td>γ-UMo-a 19.77</td>
<td>γ-UMo-b 29.25</td>
<td>U₂Mo 18.56</td>
<td>α-U 32.09</td>
<td>UC 0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray 16h</td>
<td>γ-UMo-a 14.42</td>
<td>γ-UMo-b 3.76</td>
<td>U₂Mo 36.31</td>
<td>α-U 44.27</td>
<td>UC 1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>neutron 48h</td>
<td>γ-UMo-a 14.42</td>
<td>γ-UMo-b 3.76</td>
<td>U₂Mo 36.31</td>
<td>α-U 44.27</td>
<td>UC 1.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.4: Rietveld Refinement of the diffraction patterns obtained after 500°C heat treatment; embedded are the associated 2D patterns obtained by X-ray and neutron diffraction, respectively

Table 7.6: Lattice constants of the phases $\gamma$-UMo-a, $\gamma$-UMo-b, $\alpha$-U ($\alpha'$-U, $\alpha''$-U) and $U_2$Mo for the isothermal studies at 500°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>$\gamma$-UMo-a a=b=c</th>
<th>$\gamma$-UMo-b a=b=c</th>
<th>$U_2$Mo a=b c</th>
<th>$\alpha$-U a b c</th>
<th>$\alpha$-U Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>3 h</td>
<td>3.426</td>
<td>-</td>
<td>3.425</td>
<td>10.139</td>
<td>2.869</td>
</tr>
<tr>
<td>X-ray</td>
<td>6 h</td>
<td>3.399</td>
<td>3.383</td>
<td>3.406</td>
<td>9.911</td>
<td>2.862</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>3.405</td>
<td>3.362</td>
<td>3.408</td>
<td>9.882</td>
<td>2.861</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>3.415</td>
<td>3.380</td>
<td>3.416</td>
<td>9.888</td>
<td>2.867</td>
</tr>
</tbody>
</table>
7.4 Intermediate-Temperature Reactions - 400°C, 425°C and 450°C

Table 7.7: Final agreement factors between calculated and measured data obtained by Rietveld refining the diffraction patterns for the isothermal studies at 500°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Agreement Factors</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>3 h</td>
<td>15.1 13.6 3.05 20.0</td>
<td></td>
</tr>
<tr>
<td>X-ray</td>
<td>6 h</td>
<td>5.03 6.43 1.19 29.5</td>
<td></td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>4.66 6.13 1.17 27.7</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>6.76 7.21 3.86 3.62</td>
<td></td>
</tr>
</tbody>
</table>

7.4 Intermediate-Temperature Reactions - 400°C, 425°C and 450°C

To investigate the intermediate-temperature regime, samples were annealed either at 400°C, 425°C or 450°C. Temperatures below 400°C were not examined since the focus of this work was on temperatures of 400°C and above. The following discussion will start with the studies at 450°C since the reactions will be more comparable with the high-temperature reactions.

7.4.1 Isothermal Studies at 450°C

Five samples were annealed either for 3 h ($A_{450C3h}$), 6 h ($A_{450C6h}$), 16 h ($A_{450C16h}$), 24 h ($A_{450C24h}$) or 48 h ($A_{450C48h}$). Again, X-ray and neutron diffraction methods were applied. The two samples $A_{450C3h}$ and $A_{450C16h}$ were measured with X-rays, the others with neutrons. The discussion is based on the refined diffraction patterns depicted in Figures 7.5a-7.5d and on the results obtained by Rietveld refinement listed in Tables 7.8-7.10. By inspecting the diffraction patterns, it become apparent that the measurements on specimen $A_{450C6h}$ (Figure 7.5b) do not fit in the expected order of decomposition. The diffractogram shows no indication of decomposition. Since the sample annealed for 3 h already started to decompose, the result is completely unexpected and not to explain by decomposition reactions. A possible explanation would be an erroneous preparation process where the sample was heated above the upper critical temperature after annealing. For the following discussion sample $A_{450C6h}$ will be excluded.

$A_{450C3h}$ shows that the decomposition already has started. Refining the diffraction data for this sample was difficult due to an uneven background and the presence of a lot of UC. The latter can be explained by having UC inclusions at the position of the beam spot at the experiment. Since high-energy X-ray measurements were performed only on small areas on the samples, present inclusions or grains influence the results in a way which do not represent the distribution in the total specimen. The grain structure, shown in the embedded 2D pattern in Figure 7.5a, strongly influenced the result for this measurement since it led also to a strong preferred orientation of the diffracted X-rays. Therefore, the results for the amount of $\alpha$-U and $U_2Mo$ can differ from the true value. This assumption is supported by the R-values in Table 7.10 which are, for this sample, far above the expected values for high quality refinement.

The decomposition between 16 h and 48 h can be compared with the high-temperature reactions after the same annealing durations. Since the intermediate-temperature reactions contain both, the low-temperature reactions as well as the high-temperature reactions, and due to the fact that 450°C is at the top of the intermediate-temperature regime, a comparable result to the high-temperature regime was expected for decomposition. The irregularity in the decrease of the
γ-UMo peaks and the increase of $U_2Mo$, respectively, is again due to overlapping peaks of these phases.

Table 7.9 shows the calculated lattice constants. Apparent is the small lattice parameter for γ-UMo-b after 16 h heat treatment, where the other lattice parameters for this measurement show no anomalies. Moreover, the lattice constants for the other measurements show the expected behaviour. The $\alpha$-U phase is still $\alpha'$-U.

The agreement factors in Table 7.10 show, as already mentioned above, the problems with sample A-450C3h. It is noted to compare not only the agreement factors but also the values for $Y_{obs}-Y_{calc}$, which suggest that the model fits the data pretty good.

**Table 7.8:** Crystallographic composition of U8wt.-%Mo for isothermal studies at 450°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>γ-UMo-a [wt.-%]</th>
<th>γ-UMo-b [wt.-%]</th>
<th>$U_2Mo$ [wt.-%]</th>
<th>α-U [wt.-%]</th>
<th>UC [wt.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>56.84</td>
<td>31.23</td>
<td>0.01</td>
<td>6.29</td>
<td>5.64</td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>17.74</td>
<td>21.86</td>
<td>24.10</td>
<td>35.77</td>
<td>0.53</td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>11.90</td>
<td>3.33</td>
<td>38.80</td>
<td>44.64</td>
<td>1.32</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>8.86</td>
<td>9.23</td>
<td>35.72</td>
<td>45.07</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Table 7.9:** Lattice constants of the phases γ-UMo-a, γ-UMo-b, α-U ($\alpha'$-U, $\alpha''$-U) and $U_2Mo$ for the isothermal studies at 450°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>γ-UMo-a [Å]</th>
<th>γ-UMo-b [Å]</th>
<th>$U_2Mo$ [Å]</th>
<th>α-U [Å]</th>
<th>α-U [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>3.417</td>
<td>3.393</td>
<td>3.400</td>
<td>9.890</td>
<td>2.864</td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>3.405</td>
<td>3.358</td>
<td>3.414</td>
<td>9.891</td>
<td>2.861</td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>3.403</td>
<td>3.370</td>
<td>3.415</td>
<td>9.901</td>
<td>2.868</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>3.407</td>
<td>3.379</td>
<td>3.414</td>
<td>9.925</td>
<td>2.867</td>
</tr>
</tbody>
</table>

**Table 7.10:** Final agreement factors between calculated and measured data obtained by Rietveld refining the diffraction patterns for the isothermal studies at 450°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Agreement Factors</th>
<th>$R_p$</th>
<th>$R_{wp}$</th>
<th>$R_{exp}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3 h</td>
<td>33.3</td>
<td>26.5</td>
<td>14.6</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X-ray</td>
<td>16 h</td>
<td>5.25</td>
<td>7.11</td>
<td>1.21</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>6.91</td>
<td>7.40</td>
<td>3.25</td>
<td>5.22</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>7.25</td>
<td>8.03</td>
<td>3.90</td>
<td>4.24</td>
<td></td>
</tr>
</tbody>
</table>
7.4. Intermediate-Temperature Reactions - 400°C, 425°C and 450°C

(a) $A_{450C3h}$: 3h at 450°C; high-energy X-rays

(b) $A_{450C6h}$: 6h at 450°C; neutrons

(c) $A_{450C16h}$: 16h at 450°C; high-energy X-rays

(d) $A_{450C48h}$: 24h at 450°C; neutrons

(e) $A_{450C48h}$: 48h at 450°C; neutrons

Figure 7.5: Rietveld Refinement of the diffraction patterns obtained after 450°C heat treatment; embedded are the associated 2D patterns obtained by X-ray and neutron diffraction, respectively
Table 7.11: Crystallographic composition of U8wt.-%Mo for isothermal studies at 425 °C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>γ-UMo-a</th>
<th>γ-UMo-b</th>
<th>U₂Mo</th>
<th>α-U</th>
<th>UC</th>
</tr>
</thead>
</table>
| neutron     | 3 h                | 99.06   | -       | -    | -   | 0.94
| neutron     | 6 h                | 95.12   | -       | 1.34 | 2.51| 1.04|
| X-ray       | 24 h               | 20.93   | 16.25   | 20.08| 38.93| 3.82|

7.4.2 Isothermal Studies at 425 °C

At 425 °C, three samples were annealed for either 3 h (A-425C3h), 6 h (A-425C6h) or 24 h (A-425C24h). The results of the Rietveld refinement process are depicted in Figures 7.6a and 7.6b and listed in Tables 7.11-7.13. The nucleation process is very sluggish for temperatures of 425 °C or less, and hence the decomposition starts much later as for higher temperatures. After three hours of annealing, there is still no evidence for decomposition. The composition of A-425C3h, shown in Table 7.11, is similar to the composition of A-initial discussed in Section 7.2. Therefore, after three hours of heat treatment, the sample still consists of one highly homogeneous γ-UMo.

Figure 7.6b as well as the refinement results in Table 7.11 suggest that the nucleation period is somewhere between three and six hours. A-425C6h shows a slight decomposition of the γ-UMo phase compared to A-425C3h. This becomes apparent by regarding the insets in Figures 7.6a and 7.6b. The enlarged details show that α-U and U₂Mo have already started to grow after 6 h of annealing, where there is no evidence for decomposition in sample A-425C3h. The results for A-425C24h reveal differences between the decomposition progress in the high- and intermediate-temperature regimes. Not only the nucleation but also the decomposition itself is more sluggish. After 24 hours, still a great amount of γ-UMo is left. A striking aspect is that the amount of U₂Mo is much lower compared to the results obtained after annealing at 450 °C-500 °C while the amount of α-U is only slightly lower. A retarded decomposition explains the difference in the amount of α-U but not the big difference in the U₂Mo content. Although the reactions in the intermediate-temperature regime start with a cellular reaction as in the high-temperature regime, they take a different course due to the low-temperature reactions and the formation of a Widmannstätten α-structure. These differences explain the rather high amount of α-U together with a rather low amount of U₂Mo. The amount of UC is higher then for most of the samples and can be explained again by measurement conditions at the experiment with high-energy X-rays where no homogeneous distribution of the carbides causes disproportional high amounts of UC. The lattice constants listed in Table 7.12 show no distinctive feature and the suggested α-phase is still α'-U. The agreement factors in Table 7.13 show good results even for the χ² of A-425C24h, which has been investigated with X-rays.
7.4. Intermediate-Temperature Reactions - 400 °C, 425 °C and 450 °C

(a) \( A-425C3h \): 3 h at 425 °C; neutrons

(b) \( A-425C6h \): 6 h at 425 °C; neutrons

(c) \( A-425C24h \): 24 h at 425 °C; high-energy X-rays

Figure 7.6: Rietveld Refinement of the diffraction patterns obtained after 450 °C heat treatment; embedded are the associated 2D patterns obtained by X-ray and neutron diffraction, respectively

Table 7.12: Lattice constants of the phases \( \gamma \)-UMo-a, \( \gamma \)-UMo-b, \( \alpha \)-U (\( \alpha' \)-U, \( \alpha'' \)-U) and \( \text{U}_2\text{Mo} \) for the isothermal studies at 425 °C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>( \gamma )-UMo-a ( a=b=c )</th>
<th>( \gamma )-UMo-b ( a=b=c )</th>
<th>( \text{U}_2\text{Mo} )</th>
<th>( \alpha )-U ( a )</th>
<th>( \alpha )-U ( b )</th>
<th>( \alpha )-U ( c )</th>
<th>( \alpha )-U Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>3 h</td>
<td>3.427</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>3.428</td>
<td>3.448</td>
<td>9.893</td>
<td>2.867</td>
<td>5.841</td>
<td>4.967</td>
<td>( \alpha' )</td>
</tr>
<tr>
<td>X-ray</td>
<td>24 h</td>
<td>3.418</td>
<td>3.376</td>
<td>3.407</td>
<td>9.911</td>
<td>2.863</td>
<td>5.837</td>
<td>4.952</td>
</tr>
</tbody>
</table>
7.4.3 Isothermal Studies at 400 °C

Due to the sluggish nucleation and hence a retarded decomposition at lower temperatures, only two samples were annealed at 400 °C for 24 h (A-400C24h) and 48 h (A-400C48h). Both samples were examined with neutrons. Figures 7.7a and 7.7b and Tables 7.14-7.16 summarise the results of Rietveld refinement on specimen annealed at 400 °C.

The specimen A-400C24h shows only a slight decomposition and, therefore, it was not possible to fit with a second γ-UMo phase. The most distinctive features compared to higher temperatures can be seen in Table 7.14. The increase of the rising phases is not only retarded but also starts with U₂Mo rather then with α-U. This is due to the low-temperature reactions where the decomposition is initiated by the formation of U₂Mo without the presence of α-U, whereas the latter is precipitated subsequently. Since 400 °C is still in the intermediate-temperature regime, the high-temperature reactions occur as well and ensure the formation of α-U at the very beginning of decomposition. After 48 hours, only half of the initial γ-UMo is decomposed into even parts of α-U and U₂Mo as well as some enriched γ-UMo.

The lattice parameters in Table 7.15 and the agreement factors in Table 7.16 are in good agreement with previous results and show no distinctive features. Therefore, the suggested phase for α-U is still α'-U. This has to be mentioned, since previously results by Palancher et al. found α''-U in samples with about 7 wt.% molybdenum after annealing at temperatures of 425 °C or less [37, 50]. Measurements on U8wt.-%Mo samples delivered an α'-U crystal structure. The relationship between the lattice parameters and the crystallographic structure have been discussed in their report. The same behaviour of α-U for temperature below 425 °C was observed in this work. Moreover, refining the crystal structure of α-U, which is the same for the distortion α'-U but not for α''-U, was successful and caused no problems. This induces that the specimen annealed for 425 °C and 400 °C, respectively, still contain α'-U rather then α''-U.

### Table 7.13: Final agreement factors between calculated and measured data obtained by Rietveld refining the diffraction patterns for the isothermal studies at 425 °C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Agreement Factors</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>3 h</td>
<td>$R_p$</td>
<td>8.68</td>
</tr>
<tr>
<td>neutron</td>
<td>6 h</td>
<td>$R_{wp}$</td>
<td>10.9</td>
</tr>
<tr>
<td>X-ray</td>
<td>24 h</td>
<td>$R_{exp}$</td>
<td>8.85</td>
</tr>
</tbody>
</table>

61
7.4. Intermediate-Temperature Reactions - 400°C, 425°C and 450°C

(a) A-400C24h: 24 h at 400°C; neutrons
(b) A-400C48h: 48 h at 400°C; neutrons

Figure 7.7: Rietveld Refinement of the diffraction patterns obtained after 400°C heat treatment; embedded are the associated 2D patterns obtained by X-ray and neutron diffraction, respectively

Table 7.14: Crystallographic composition of U8wt.-%Mo for isothermal studies at 400°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Weight Fraction [wt.-%]</th>
<th>(\gamma)-UMo-a</th>
<th>(\gamma)-UMo-b</th>
<th>(U_2)Mo</th>
<th>(\alpha)-U</th>
<th>UC'</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>83.23</td>
<td>-</td>
<td>10.55</td>
<td>4.50</td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>46.84</td>
<td>7.59</td>
<td>22.08</td>
<td>22.72</td>
<td>0.76</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.15: Lattice constants of the phases \(\gamma\)-UMo-a, \(\gamma\)-UMo-b, \(\alpha\)-U (\(\alpha'\)-U, \(\alpha''\)-U) and \(U_2\)Mo for the isothermal studies at 400°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Lattice Constants [Å]</th>
<th>(\gamma)-UMo-a</th>
<th>(\gamma)-UMo-b</th>
<th>(U_2)Mo</th>
<th>(\alpha)-U</th>
<th>(\alpha)-U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a=b=c</td>
<td>a=b=c</td>
<td>a=b</td>
<td>c</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>neutron</td>
<td>24 h</td>
<td>3.427</td>
<td>3.436</td>
<td>9.923</td>
<td>2.866</td>
<td>5.867</td>
<td>4.955</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td>3.427</td>
<td>3.387</td>
<td>9.931</td>
<td>2.867</td>
<td>5.851</td>
<td>4.956</td>
</tr>
</tbody>
</table>

Table 7.16: Final agreement factors between calculated and measured data obtained by Rietveld refining the diffraction patterns for the isothermal studies at 400°C

<table>
<thead>
<tr>
<th>Examination</th>
<th>Annealing Duration</th>
<th>Agreement Factors</th>
<th>(R_p)</th>
<th>(R_{wp})</th>
<th>(R_{exp})</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron</td>
<td>24 h</td>
<td></td>
<td>12.7</td>
<td>14.0</td>
<td>3.15</td>
<td>19.7</td>
</tr>
<tr>
<td>neutron</td>
<td>48 h</td>
<td></td>
<td>6.75</td>
<td>6.99</td>
<td>3.46</td>
<td>4.09</td>
</tr>
</tbody>
</table>
In the following sections of this chapter, the results obtained at Stress-Spec during in-situ annealing will be presented and discussed. The main objective of this measurement was the determination of the beginning of phase decomposition along with the observation of the growths of the individual peaks. Calculating the exact crystallographic composition as a function of in-situ annealing duration was not performed. There are two major reasons which make Rietveld refinement less accurate and, therefore, not comparable with previous measurements. First, a small angular range compared to experiments at Spodi and Hems, respectively. Second, a relatively low statistics due to short term measurements. Therefore, the results obtained by in-situ annealing measurements complement the results for crystallographic phase composition. Again, the measurements are divided into high- and intermediate-temperature reactions.

8.1 Data Analysis

The consecutive collected diffraction patterns have been analysed with the StressTextureCalculator [51]. This software sequentially processes all diffraction patterns. It corrects the detector image via a dark measurement (see Chapter 6.3.1), allows to subtract the background and offers several possibilities for fitting the peaks.

Diffraction patterns were collected in an angular range from $2\theta = 37.8^\circ$ to $56.7^\circ$, which corresponds to $\sin(\theta)/\lambda = 0.17\ \text{Å}^{-1}$ to $0.25\ \text{Å}^{-1}$. This range has been chosen due to the fact that the most distinctive peaks of each individual phase lie inside this range. Therefore, it is theoretically possible to observe the following peaks (peaks in brackets are overlapping with other peaks; peaks in square brackets were not observable; peaks without brackets are unaffected by other peaks):

- $\gamma$-UMo phase: $(\gamma_{110})$
- $\alpha$-U phase: $[\alpha_{020}]; \ \alpha_{110}; \ (\alpha_{021}); \ (\alpha_{002}); \ \alpha_{111}$
- $U_2$Mo phase: $(U_2\text{Mo}_{004}); \ (U_2\text{Mo}_{110}); \ (U_2\text{Mo}_{103}); \ [U_2\text{Mo}_{112}]$

The peaks $\alpha_{020}$ and $U_2\text{Mo}_{112}$ have a very low intensity which disappears in the background, and hence these peaks could not be observed. Moreover, due to the overlap of the peaks $\gamma_{110}$, $U_2\text{Mo}_{110}$ and $U_2\text{Mo}_{103}$, it was not possible to observe the correct peak intensity increase and decrease, respectively, of these peaks. It should be noted that a second $\gamma$-UMo phase was not included into the evaluation since it is not possible to distinguish a second $\gamma$-phase at about the
8.1. Data Analysis

same position as the first one. Also the peaks \( \alpha_{021} \), \( \alpha_{002} \) and \( U_{2\text{Mo}_{0.04}} \) are overlapping each other. Since all of them are increasing with time, at least the start of phase decomposition could be observed. Due to the above mentioned short term measurements and small angular range, the exact content of \( \alpha \text{-U} \) via Rietveld refinement could not be calculated. Therefore, it was not possible to determine the intensities of the single phases \( \alpha_{021} \) and \( \alpha_{002} \) and hence an estimated intensity for \( U_{2\text{Mo}_{0.04}} \). Nonetheless, all peaks can be observed qualitatively by regarding the collected diffraction patterns as a function of time.

The peak growth of a single peak was determined by observing the sum of intensities over an angular range as a function of time. Thereby, the angular range is the same for all diffraction patterns of one sequential measurement. This method was preferred over fitting each individual peak since the fit was not good for very small peaks, i.e. the beginning peak growth.

The obtained peak growth curvatures were then analysed with the Avrami equation introduced in Chapter 3.1. A modified Avrami equation is derived out of Equation 3.1 and gives the intensity as a function of time, i.e. \( I(t) \):

\[
I(t) = \begin{cases} 
A(1 - \exp(-k(t-t_0)^n)) + B & ; t > t_0 \\
B & ; t \leq t_0 
\end{cases}
\]

(8.1)

where, beside the above described parameters, \( A \) is a scale factor for the intensity, \( B \) describes the background intensity and \( t_0 \), with a lower limit of \( t_0 = 0 \), was introduced in order to describe peak growth curvatures which not start at \( t = 0 \). The latter is the rule rather than the exception since the region needs some time to nucleate before starting to grow a new phase. This is not covered by the original Avrami equation 3.1 which only describes the growth. Thereby, \( t_0 \) does not describe the induction period for nucleation but is only an auxiliary variable for the fitting process. With the obtained fit parameter by fitting Equation 8.1 into the data, the onset of peak growth \( \tau \) as well as the end of peak growth \( \tau_e \) can be derived. Since \( \tau \) and \( \tau_e \) are defined by the intersection of the linear part of the growth curve with the background and saturation, respectively, an uniform definition for the linear part was required. In this work, the tangent through the point of inflection of the S-shaped Avrami curve is taken as the linear part. Both, the background \( B \) and the saturation \( (A + B) \) are given by the fit and, therefore, \( \tau \) and \( \tau_e \) can be calculated. The uncertainty for these were derived by calculating the propagation of uncertainty and taking into account the covariance, since the variables obtained by fitting the data are correlated. Tables C.1-C.4 summarise the fit parameters and the derived results. Since the fit parameter will be discussed only marginally, the tables are only attached in Appendix C. Figure 8.1 shows the Avrami equation fitted into an exemplary data plot with the most important characteristics drawn in.

Diffraction patterns were not only collected during isothermal annealing but also during the heating. A Gaussian fit into the main \( \gamma_{110} \)-peak delivers the peak position as a function of the temperature. Hence, the thermal expansion coefficient for \( \gamma \text{-UMo} \) could be determined. Overlapping peaks at this position have not to be taken into account, since the \( \gamma \)-phase is not yet decomposed and, therefore, no other peaks exist. In a final step the transition into the high-temperature phase was observed by heating an already decomposed sample up to 650°C.
It should be mentioned that, due to experimental limitations, the specimen was not heated instantly to the desired temperature but heated with a certain rate. It was chosen to heat with 10°C/min in order to avoid an overshoot of the temperature. The effect caused by the heating process is negligible, since the time spent in the temperature regime where decomposition starts early is rather short.

8.2 High-Temperature Reactions - 475°C, 500°C and 525°C

For the investigation of the reaction kinetics in the high-temperature regime, three highly homogeneous γ-U8wt.-%Mo samples were measured during in-situ annealing at either 475°C, 500°C or 525°C. Moreover, a sample already treated for 16h at 500°C was examined during in-situ annealing for another 20h at 500°C in order to observe later phase decomposition. The following discussion will start with the measurements at 500°C, as most features can be shown and explained on the basis of these in-situ annealing studies.

8.2.1 Isothermal In-Situ Annealing Studies at 500°C

The specimen was annealed for 7h at 500°C and diffraction patterns were collected every 5 min. The sequential collected diffractograms obtained at STRESS-SPEC are shown in Figure 8.2. The waterfall chart shows the decomposition of the γ-UMo phase in steps of 25 min. Moreover, the

![Figure 8.1: Avrami fit into an exemplary data plot; the fit delivers the background B, the saturation (A+B) and the tangent to the inflection point, from which τ and τe could be derived](image-url)
beginning and end of the \( \alpha \)-U peak growth are depicted in red. The beginning of the \( \alpha \)-phase growth is also the beginning of the phase decomposition, since \( \alpha \)-U is, together with \( \text{U}_2\text{Mo} \), the first product of intermediate- and high-temperature reactions. The information on beginning and end of peak growth are obtained by observing the peak intensities as a function of time. Thereby, the most promising peaks are \( \alpha_{110} \) and \( \alpha_{111} \) due to the fact that these are the only peaks which do not overlap with any other. Also observable are the peaks \( \alpha_{021}/002 \) which are seen as one peak since it is not possible to distinguish between them. Both peaks are growing equally and hence the result for the start of phase decomposition, obtained by observing the peak growths together, is correct. It should be mentioned that the varying peak heights before decomposition are due to a noticeable grain structure in the \( \gamma \)-phase. Since the sample was rotated during measurements and the grain structure leads to a preferred orientation, varying intensities are observable. During annealing, and hence during decomposition, the grain structure becomes smaller and therefore the effect of preferred orientation vanishes.

Figures 8.3a, 8.3b and 8.3c show the growth of the \( \alpha \)-peaks along with the fits for the Avrami equation and the resulting tangent through the point of inflection, the background and the saturation. It is shown that the used model describes the obtained data well. Table C.2 summarises the parameters for the Avrami fit along with the derived results. Taking the mean value of \( \tau \) and \( \tau_e \) in the three observed growth curvatures gives the nucleation period \( \tau \) and the end of peak growth \( \tau_e \), respectively:

\[
\tau = (135.41 \pm 3.75) \text{ min} \quad \tau_e = (336.46 \pm 1.49) \text{ min}
\]
8. Phase Decomposition Measurements During In-Situ Annealing

By regarding the peak growth curvatures along with the straight lines it becomes apparent that the nucleation period $\tau$ and end of peak growth $\tau_2$; (d): red data points describe the fast growth shown in more detail in Figure 8.3a; blue data points were obtained by in-situ annealing studies of a sample pre-annealed for 16h at 500°C

Sample A-500C16h, which has already been measured with HE-XRD, was in-situ annealed for another 20h at 500°C and diffraction patterns were collected every 5 min. Figure 8.3d shows the $\alpha_{110}$-peak intensities for the measurements from 16-36 h together with the measurements from 0-6h. It can easily be seen, that the saturation described by the Avrami curve does not
8.2. High-Temperature Reactions - 475 °C, 500 °C and 525 °C

exactly define the end of peak growth. After the fast growth described by the Avrami curve, the peak keeps on growing slowly with a linear like rise. According to this, the Avrami theory does not describe the peak growth in UMo exactly, but describes the fast growth, until reaching the point where the linear like growth starts, pretty well. For further discussions the Avrami curve describes always this fast growth at the beginning of phase decomposition rather then the total peak growth. This will later be of much importance for the discussion and complementation of the data obtained from diffraction patterns and peak growth curvatures, respectively.

8.2.2 Isothermal In-Situ Annealing Studies at 525 °C

Although for crystallographic phase analysis no sample was prepared at 525 °C, in-situ annealing studies were performed at this temperature. The idea was to investigate the further development in the beginning of phase decomposition, since the minimum time period for this was expected to be between 475 °C and 525 °C. Phase transformation could be observed in less then 2h, and hence the total annealing time was set to 4.5h. Diffraction patterns were collected every 5 min.

The development of the diffraction patterns as a function of annealing time is again depicted as a waterfall chart in Figure 8.4. Noteworthy is that the $\gamma$-UMo peaks before the start of decomposition are similar, what can be explained by the absence of a noticeable grain structure. Due to a total annealing time of only 4.5h, the end of peak growth for $\alpha$-U was narrowly missed as could be seen only later by analysing the peak growth curves. By regarding only the data of the $\alpha$-peaks shown in Figures 8.5a to 8.5c, the curve already bends at the end of annealing and becomes its sigmoidal shape. With the fit parameters in Table C.1, it was possible to derive not only $\tau$ but also $\tau_e$, even though $\tau_e$ is not within the measured time period. The average value for the nucleation period and the end of peak growth is determined to

$$\tau = (98.77 \pm 4.52) \text{ min} \quad \tau_e = (274.02 \pm 3.18) \text{ min}$$

and depicted red in the waterfall chart (Figure 8.4).
8.2.3 Isothermal In-Situ Annealing Studies at 475°C

For the study at 475°C, a sample was annealed for 10h, whereby diffraction patterns were collected every 5min. Here again, the waterfall chart in Figure 8.6 represents the peak growth as a function of time at 475°C. This sample had a comparable grain structure to the sample annealed at 500°C, which can be seen in the varying peak heights before the start of decomposition. The results for fitting the Avrami equation into the data sets in Figures 8.7a to 8.7c yield

\[ \tau = (348.08 \pm 18.99) \text{ min} \]

\[ \tau_e = (815.98 \pm 25.19) \text{ min} \]

which is against the expectations that the times for the start of phase decomposition are on a C-shaped curve in the TTT-diagram. For the following discussion, the nucleation rate obtained during in-situ measurements at 450°C (Chapter 8.3.1) needs to be given already here. Comparing \( \tau \) and \( \tau_e \) obtained at 450°C, 475°C and 500°C,

\[ \tau_{450°C} = (232.03 \pm 2.95) \text{ min} \]
\[ \tau_{475°C} = (348.08 \pm 18.99) \text{ min} \]
\[ \tau_{500°C} = (135.41 \pm 3.75) \text{ min} \]

\[ \tau_{e450°C} = (510.73 \pm 1.11) \text{ min} \]
\[ \tau_{e475°C} = (815.98 \pm 25.19) \text{ min} \]
\[ \tau_{e500°C} = (336.46 \pm 1.49) \text{ min} \]

show that for 475°C the phase decomposition starts at the latest. Since, in a TTT-diagram the start of decomposition lies on a C-shaped curve, the nucleation rate for 475°C should lie in between or before the times required for nucleation at 500°C and 450°C. The same applies for
the end of peak growth. An explanation for such a delayed onset of phase decomposition is a difference between the measured temperature and the real temperature at the sample position. The measurement of a lead(II) titanate (PbTiO$_3$) performed at STRESS-SPEC showed that the temperature inside the high-temperature vacuum furnace strongly depends on the position inside the furnace. During this test, a vanadium tube was filled with PbTiO$_3$ and heated inside the high-temperature furnace. Since this standard performs a phase transition at about 475°C, the temperature at the sample could be determined. It was shown that the temperature at the thermocouple deviates strongly from the sample’s temperature at a different position, depending on the distance between sample and thermocouple. Therefore, although the samples always were placed on the central axis of the cylindrical heating element, a temperature gradient could be observed along this axis. To manage this problem the thermocouple and the sample were in direct contact, only separated by a thin vanadium foil. If, during installation of the specimen carrier into the furnace, the sample gets shifted away from the thermocouple, a difference in temperature can be present. The value for $\tau_{475^\circ C}$ indicates a temperature between 425°C and

Figure 8.5: Growth of the $\alpha$-peaks during annealing at 525°C as a function of the annealing time; intersection of the linear portion fits with the background defines the nucleation period $\tau$.
Figure 8.6: Waterfall chart of the γ-UMo phase decomposition as a function of the annealing time at 475 °C; diffraction pattern at the beginning of phase decomposition is shown in red

450 °C, based on further investigations at 425 °C.

The contention that the temperature at the sample was not 475 °C is not only based on the above mentioned reasons but also on the peak growth curves in Figures 8.7a to 8.7c. Another explanation for a delayed nucleation would be that the temperature at the sample was reached at a later point in time. This can be invalidated by taking the slope of the tangent through the inflection point into account. Assumed that the temperature at the sample was 475 °C, reached not at the beginning of measurement but to a later time, the slope would lie between the slope obtained at 500 °C and 450 °C. This is because not only the nucleation rate is on a C-shaped curve but also the time of finishing the peak growth. Thereby, the slope determines the time required for completing a peak growth. Comparing the fit parameters in Table C.3 for 475 °C with the parameters for 500 °C (Table C.2) and 450 °C (Table C.4), respectively, shows that the slope for the α-peak growths at 475 °C is lower then for 500 °C and 450 °C. Thus, the assumption that the temperature was lower than 475 °C, rather then only reached to a later time, is supported.
8.3 Intermediate-Temperature Reactions - 450 °C and 425 °C

To investigate the intermediate-temperature regime, two highly homogeneous γ-U8wt.%Mo samples were measured during in-situ annealing at either 450 °C or 425 °C. Lower temperatures were not considered, since measurements at SPoDi showed that the decomposition only begins after long annealing durations which would have exceeded the available beam time at STRESS-SPEC.

8.3.1 Isothermal In-Situ Annealing Studies at 450 °C

The sample was annealed for 10h at 450 °C and diffraction patterns were collected every 5 min. The diffraction patterns as a function of annealing time are depicted in the waterfall chart shown in Figure 8.8. Once more the grain structure in the specimen results in varying peak intensities before decomposition. The obtained data along with the Avrami fit for the observed α-U phases are shown in Figures 8.9a-8.9c and the fit parameters are attached in Table C.4.
Figure 8.8: Waterfall chart of the $\gamma$-UMo phase decomposition as a function of the annealing time at 450°C; diffraction patterns at the beginning and end of decomposition, respectively, are shown in red.

The results deliver

$$\tau = (232.03 \pm 2.95) \text{ min} \quad \tau_e = (510.73 \pm 1.11) \text{ min}$$

8.3.2 Isothermal In-Situ Annealing Studies at 425°C

As a final investigation of the intermediate-temperature regime, a specimen was annealed for 10 h at 425°C. After 10 h of annealing only the first signs of decomposition are visible as can be seen in Figure 8.10a. Whereas, the differences are barely visible by regarding the total collected diffraction patterns, the magnified area shows more details. The $\alpha$-peaks as well as the U$_2$Mo-peak starts to grow, while the $\gamma$-peak decreases. Moreover, the growth of the $\alpha$-peak intensities shown in Figures 8.10b and 8.10b show the very beginning of peak growth and hence of the nucleation. The collected data was not sufficient for the Avrami fit and, therefore, nucleation period and end of peak growth could not be determined.

Noteworthy is that for all Avrami fits $n \approx 3$ within the margin of error, whereas for a three-dimensional nucleation and growth process $n \geq 3$. For zero nucleation rate it is $n = 3$ and for a decreasing nucleation rate it is $3 < n < 4$. Therefore, the results suggest either a zero or decreasing nucleation rate. The data obtained by the Avrami fit comprises a lot of information concerning the peak growth and nucleation which has not been evaluated within the framework of this thesis. An outlook towards this is given in Chapter 10.2. Moreover, the theory of nucleation...
8.3. Intermediate-Temperature Reactions - 450 °C and 425 °C

---

**Figure 8.9:** Growth of the α-peaks during annealing at 450 °C as a function of the annealing time; intersection of the linear portion fits with the background and saturation, respectively, define the nucleation period \( \tau \) and end of peak growth \( \tau_e \).

and phase growth can be found in *The Theory of Transformation in Metals and Alloys - Part I/II* by Christian [30, 31].
Figure 8.10: Diffraction patterns and growth of the $\alpha$-peaks during annealing at 425 °C as a function of the annealing time.
8.4 High-Temperature Phase Transition

In order to observe the transition into the high-temperature $\gamma$-phase, the sample decomposed for 4.5 h at 525 $^\circ$C was heated from 525 $^\circ$C to 650 $^\circ$C, i.e. above the critical temperature, and diffraction patterns were collected every minute. Figures 8.11a and 8.11b show the phase behaviour during the heating process. Thereby, the diffraction patterns in Figures 8.11a show that the decomposition over several hours retrogresses in a few minutes.

The growth of $\alpha$-U, i.e. $\alpha_{110}$-, $\alpha_{111}$- and $\alpha_{021/002}$-peaks, is depicted in Figure 8.11b. All peaks vanish within the same time interval of about 8 min. Although this phase transition should occur instantaneous, a process comparable to the growth of a peak is present. This is explained by the facts that the transformation does not take place everywhere in the bulk sample simultaneously and the transformation itself takes some finite time.

Determining the critical temperature, i.e. above this point only the high-temperature $\gamma$-phase is present, was complicated. The data suggests that the retrogression starts somewhere between 600 $^\circ$C and 625 $^\circ$C, whereas the value was expected to be below 600 $^\circ$C. The discrepancy compared to $T_{crit}=587^\circ$C found in literature [38] has two major reasons. First, the heating rate was chosen to be 5 $^\circ$C/min what turned out to be too high, thus the specimen could not adopt to the set temperature while the thermocouple already was on a higher temperature. The measurement can be improved by heating the sample stepwise and holding it after each step on the elevated temperature. This approach ensures that the sample adepts the temperature and, therefore, shows at which step the retrogression takes place. Second, diffraction patterns were collected every minute and hence details in the diffraction pattern could be lost.

Another method for determining the critical temperature more accurately will be presented in Chapter 10.2.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffraction_patterns.png}
\caption{(a) Diffraction patterns along the transition process
\hspace{1cm} (b) $\alpha$-peak shrinking as a function of temperature and time}
\end{figure}

\textit{Figure 8.11: Transition into the high-temperature $\gamma$-phase}
8.5 Coefficient of Thermal Expansion for $\gamma$-UMo

Measurements during the heating process of the samples delivered information for the determination of the thermal expansion coefficient of the $\gamma$-UMo phase. Gaussian fits into the $\gamma_{110}$-peak of each sequentially collected diffraction pattern give the peak position as a function of the temperature. With Equation 4.4 and Equation 4.5, the Bragg peak position directly defines the lattice parameter for a cubic lattice system:

$$
a = \frac{\lambda}{\sqrt{2} \sin \theta_{110}} \pm \frac{\lambda \cos \theta_{110}}{\sqrt{2} \sin^2 \theta_{110}} \Delta \theta_{110} \quad (8.2)
$$

Therefore, Figure 8.12 shows the lattice parameter of the $\gamma$-UMo phase as a function of time for two different heating processes, i.e. 50-490°C and 50-460°C. The thermal expansion coefficient is determined, according to Equation 2.4, with the slope of the linear fit through the data points and the lattice parameter at the beginning of heating to

$$
\alpha_{50-490^\circ C} = (14.23 \pm 0.20) \cdot 10^{-6} \frac{1}{K} \\
\alpha_{50-460^\circ C} = (14.30 \pm 0.51) \cdot 10^{-6} \frac{1}{K}
$$

These results are comparable to results for U9wt.-%Mo and U10wt.-%Mo alloys, respectively, found in literature [52–54]:

$$
\alpha_{20-500^\circ C} = 15.22 \cdot 10^{-6} \frac{1}{K} \quad \text{U9wt.-%Mo; [52, 53]} \\
\alpha_{RT-500^\circ C} = (15.6 \pm 2.2) \cdot 10^{-6} \frac{1}{K} \quad \text{U10wt.-%Mo; [54]}
$$

Due to the noticeable grain structure in some samples and the rotating experimental set-up, the peak position reciprocates as a function of time. The effect can be seen by observing the measurement for the heating process 50-460°C in Figure 8.12. This effect is more significant in other samples and, therefore, needs to be corrected in order to evaluate these data. Since thermal expansion coefficients are only a spin-off product of in-situ annealing measurements and not the scope of this work, no further discussion on the obtained data is given.
Figure 8.12: Lattice parameter of the $\gamma$-UMo phase as a function of the temperature
In this chapter, all results obtained for phase decomposition are summarised in order to achieve an isothermal transformation diagram for U8wt.-%Mo in the observed time and temperature range. While the performed in-situ annealing measurements determined the onset of phase decomposition, diffraction patterns at different points in time and temperature were used to derive the crystallographic phase composition at these points. Hence, in-situ measurements gave information on the time a phase starts to decompose, but not on the exact crystallographic composition as a function of time. Crystallographic phase analysis, on the other hand, delivered detailed information on the phase composition in U8wt.-%Mo at a certain time and temperature, but none about how this state was reached. Therefore, a complementary consideration of both methods is required. The following discussion will start with the results from in-situ annealing studies and their contribution to the TTT-diagram, which will be subsequently complemented by the crystallographic phase analysis studies.

9.1 Contribution of the Individual Methods

Different definitions for start and end of phase decomposition define the positioning of the C-shaped curves in a TTT-diagram. As already discussed in Chapter 3, earlier work used first signs of phase decomposition for defining transition curves, while the definition via growth curvatures can be found in current literature. Both can be extracted from the data obtained during in-situ annealing.

Comparing the growth curvatures with the data for crystallographic composition of annealed samples shows, that, after the fast growth of a peak has stopped at \( \tau_e \), the peaks keep growing with a linear like behaviour and much slower compared to the fast growth. The latter statement is supported by the peak growth behaviour observed at 500 °C discussed in Chapter 8.2.1, where not only the fast growth was observed but also the growth for \( t > \tau_e \). This linear like growth of a peak approaches slowly the saturation of this phase. The time when the fast growth reaches the linear like growth cannot be determined exactly, since the measurements were not performed over such a long period. Therefore, it was destined to be 99% of the fast peak growth and, hence, can be calculated with the Avrami equation for each certain temperature. Moreover, the ‘first sign of phase decomposition’ was chosen to be 1% of the fast peak growth. Another crucial point is 50% of phase growth, which is defined by the point of inflection determined by the Avrami fit. Noteworthy is that the times \( \tau \) and \( \tau_e \), defined in Chapter 8.1, are calculated to be about 10%
9.1. Contribution of the Individual Methods

and 90% of the fast peak growth.

To sum up, following information for the TTT-diagram is obtained by in-situ annealing studies:

- $t_0$: first signs of phase decomposition, i.e. 1% of the $\alpha$-peak fast growth
- $\tau$: start of phase decomposition according to the definition via Avrami curves
- $t_{50\%}$: 50% of the fast growth is reached, i.e. point of inflection
- $\tau_e$: end of phase decomposition according to the definition via Avrami curves
- $t_e$: start of the linear like rise after fast growth is finished, i.e. 99% of the $\alpha$-peak fast growth

The contribution of in-situ annealing studies to the isothermal transformation diagram is depicted in Figure 9.1. Plotted are the above described times describing the fast growth of $\alpha$-U and, hence, the beginning of phase decomposition along with detailed information on $\alpha$-U growth. Due to the limitations in analysing all peaks within the angular range, the fast growth of $U_2$Mo was not observed quantitatively. Nonetheless, since $\alpha$-U is, together with $U_2$Mo and a second $\gamma$-phase, the first product of $\gamma$-UMo phase decomposition, the start of transformation is described well by observing the $\alpha$-peak. As already discussed in Chapter 8.2.3, the measurement at 475°C was erroneous and therefore is not considered for the final result.
Figure 9.1: Isothermal transformation curves describing the fast growth of $\alpha$-U in U8wt.-%Mo.
9.1. Contribution of the Individual Methods

The information obtained by crystallographic phase analysis contributes less significant to the C-curves for beginning of phase decomposition in the TTT-diagram. This has its reasons in the wide distribution of the measuring points in time. Although measurements at 3h and 6h at a certain temperature were not sufficient to observe the fast growth of peaks, measuring points between \( t_0 \) and \( t_e \) can yet be used to complement the fast growth curves and support the results obtained by in-situ annealing studies.

Analysing severely decomposed material, on the other hand, gives insight on how advanced the phase decomposition is. The data suggests that the fast growth for \( \text{U}_2\text{Mo} \) and \( \alpha\text{-U} \) starts together but rises differently. The fast growth of \( \text{U}_2\text{Mo} \) takes much longer. Comparing the data obtained for measurements on samples annealed for 24h and 48h, respectively, for the temperature between 450°C and 475°C, suggests that \( \text{U}_2\text{Mo} \) keeps growing with a linear like rise after the fast growth. Therefore, the data indicate the latest end of the \( \text{U}_2\text{Mo} \) fast growth and therefore the points after which the content of the transformation products increases only slightly with time. An exact determination of this transformation curve is not possible due to the fact that measurements were only performed for 16h and 24h, and not somewhere in between. Thus, a C-shaped area describing the latest end of \( \text{U}_2\text{Mo} \) fast growth and the approach of the end of phase decomposition can be estimated. Figure 9.2 shows the isothermal transformation curve describing the latest end of \( \text{U}_2\text{Mo} \) fast growth along with the measuring points and their determined crystallographic composition. Thereby, the dashed part of the curve describes an estimation, since no sample was prepared at 425°C and 48h annealing as well as for times greater then 48h at 400°C.

Figure 9.3 comprises the curves from Figure 9.1 and Figure 9.2 and therefore gives the final TTT-diagram. Thereby, the diagram shows the start of the cellular reaction where \( \gamma\text{-UMo} \) starts to transform into \( \alpha\text{-U} \) and \( \text{U}_2\text{Mo} \), the end of the \( \alpha\text{-phase fast growth} \), the latest end of the \( \text{U}_2\text{Mo} \) fast growth and the region where the remaining \( \gamma\text{-UMo} \) slowly vanishes as the \( \alpha\text{-U} \) and \( \text{U}_2\text{Mo} \) rise with a linear like behaviour.
Figure 9.2: Isothermal transformation curves describing the region where the latest end of $U_2$Mo fast growth in U8wt.-%Mo is
9.1. Contribution of the Individual Methods

Figure 9.3: Isothermal transformation diagram of U8wt.-%Mo
9.2 Comparison with Previous Results

The results of this work can be compared to the previous results found in literature. Figure 9.4 shows the isothermal transformation curves obtained in this work drawn into the TTT-diagram for U8wt.-%Mo proposed by Repas et al. in 1964 [38]. It should be noted in advance that the transformation curves in the literature were obtained by preparing a grid of samples and examine them via metallurgical methods and with dilatometric, microhardness and xrd data. Thereby, an exact definition for the start of phase decomposition was not obvious. Moreover, the number of measurement points, and therefore the density of the measurement grid, is not given. Due to these reasons, the accuracy and reliability of their TTT-diagram has to be treated with some caution.

A significant difference can be seen by regarding the start of the cellular reaction. Thereby, it looks like the transformation curve is shifted by about 25 °C compared to the earlier results. The question rises whether the temperature was monitored wrong or the start of cellular reaction was defined significant differently by Repas et al. For further comparisons it is necessary to discuss that the examination at 475 °C were erroneous and the results suggested a lower temperature during this measurement. Therefore, no reliable information for the TTT-diagram were obtained for 475 °C, which would have been valuable for the discussion. The other measurements are compatible to each other and showed the expected behaviour. The measurement of a PbTiO₃ standard performed its phase transition at the correct temperature what invalidates the suspicion of a wrong monitoring of the temperature during all the measurements. As will be pointed out later in Chapter 10.2, measurements at 475 °C should be repeated in order to regain the lost information at this temperature and, moreover, to verify the temperature.

The isothermal transformation curves obtained in this work contains information on the fast growth of α-U. The C-shaped curvatures for 50% and 99% fast growth, respectively, can not be compared to older measurements since these do not contain this information. The data show that the fast growth for U₂Mo is much slower compared to the fast growth for α-U. Despite the suggestions from the literature where first the α-U precipitates and U₂Mo start to grow later, the data obtained by Rietveld analysis showed that both transformation products start to grow simultaneously. Thereby, the C-shaped area in the rearward of the diagram describes the end of the U₂Mo fast growth and the approach of the end of phase decomposition. A 100% transformation of the metastable γ-UMo could not be seen within 48 h of annealing at any temperature. Information on the crystal habit of the formed transformation products were not obtained, since diffraction data was used to determine the phase composition rather then metallurgical methods.
9.2. Comparison with Previous Results

Figure 9.4: Isothermal transformation curves obtained in this work and compared to the diagram obtained by Repas et al. [38]
Part IV

Conclusion
CHAPTER 10

Summary and Outlook

The objective of the thesis was the investigation of the isothermal transformation kinetics in an uranium-molybdenum alloy with a molybdenum content of 8wt.-%. Thereby, the project’s focus was on temperatures between 400°C and 525°C for annealing durations of up to 48h. The motivation was to estimate the phase composition inside an U8wt.-%Mo nuclear fuel after treated on elevated temperatures during the production process of the fuel element.

10.1 Summary

For the measurements, a total number of 26 samples were prepared. Therefore, pieces were cut down from an ingot of depleted U8wt.-%Mo with a diamond wire saw and melted with an electric arc furnace. The specimen were then annealed for different times at different temperatures in order to prepare a grid of measurement points. For an initial assessment of the quality, surface preparation steps were conducted on a few samples and SEM measurements were performed.

One of the two primary series of experiments were the crystallographic phase analysis of specimens annealed at different temperatures and times. Measurements were performed with neutron diffraction on Spodi at the FrM II, as well as with high-energy X-ray diffraction on HEMS at the DESY. Thereby, quantitative information on the crystallographic composition of the samples as a function of time and temperature was determined.

The other main experiments were in-situ annealing studies on pure γ-UMo and decomposed material, respectively, at different elevated temperatures. Measurements were performed with neutron diffraction on STRESS-Spec at the FRM II. At this point, one major advantage of neutron diffraction over X-ray diffraction is at hand: The neutrons easily penetrate the complex experimental set-up with the high-temperature vacuum furnace. As a result, quantitative information on the fast growth of α-U as well as qualitative information on the behaviour of γ-UMo and U₂Mo was obtained.

The obtained results were then combined in order to achieve an isothermal transformation diagram (TTT-diagram) for U8wt.-%Mo in the observed time and temperature range.
10.2 Outlook

In addition to the methodology chosen in this thesis, several other options are available to achieve the same goals or complement these results. Moreover, various spin-off data from the measurements were collected, which have not yet been evaluated. This chapter summarizes the outlook on different projects that could follow up this work.

10.2.1 High-Temperature Phase Transition via Differential Scanning Calorimetry

The concept for a feasibility study for the measurements of high-temperature phase transitions via differential scanning calorimetry developed as a joint project of this work and the work by Reiter [55].

Differential scanning calorimetry measures the heat required to increase the temperature of a sample compared to a reference material as a function of temperature. Thereby, this method gives the change of heat capacity as a function of temperature. Phase transitions can be detected since the heat flow to the sample will be higher or lower as to the reference material, depending on the transition. The device used to perform the experiment is a Perkin Elmer DSC 8500 which has been calibrated for temperatures around 575 °C with a KaSO₄ standard. The idea was to heat decomposed UMo samples and determine not only the temperature where the high-temperature phase transition starts but also the energy required for the retrogression from the decomposed material to the γ-UMo. In the following, only the already performed feasibility study is presented.

In total three samples were measured which have already been decomposed for either 6h at 500 °C or 16h at 475 °C. Thereby, two slices of sample A-475C16h and one slice of sample A-500C6h were investigated. Figure 10.1 shows the heat flow as a function of temperature for sample A-475C16h collected with the dsc. For this feasibility study, the critical temperature has been determined using the instrumental software. This software determines the intersection of the point of inflection of the ascent and the interpolation between two arbitrarily chosen points on the background. For further investigations a more reliable scientific definition needs to be found. Nonetheless, with the results from the first calculations for the critical temperature and the enthalpy of phase transition, respectively, the feasibility of this method is shown.

Further experiments should include the calibration of the DSC over the total range of temperature, measurements of samples with various stages of decomposition and the execution with different heating rates. Therefore, not only the critical temperature for UMo but also the correlation between the stage of decomposition and the required heat for retrogression can be determined.

10.2.2 Additional Data Obtained by In-Situ Annealing Studies

By performing the in-situ measurements, an angular range including several peaks was observed during heating, cooling and isothermal processes. Therefore, a large amount of data was collected which has not yet been evaluated:
While most studies started with pure $\gamma$-UMo samples, the heating process for these measurements delivered only information on the $\gamma_{110}$-peak. Therefore, the thermal expansion coefficient discussed in Chapter 8.5 could be determined.

During the investigation of an already decomposed UMo sample, the peak positions as a function of temperature was collected for all peaks within the angular range. Observing the cooling processes also delivered information on several peaks within the angular range, since at this time the sample was already decomposed. The collected data makes it possible to determine the thermal expansion coefficient not only for the $\gamma$-phase but also for all other observed phases.

The in-situ annealing studies at 425°C for 10h showed only minor indications for phase decomposition. However, the $\gamma$-peak position and width as a function of time comprise the information on the precipitation of the $\gamma$-UMo-b phase as a function of time at this certain temperature.

Measurements performed at 500°C for $t > \tau_c$ were not fully investigated and, hence, more information on how the peak growth continues after finishing the fast growth described by the Avrami curve can be obtained.

It might be possible to analyse each individual peak, even the peaks which overlap each other, by sequential Rietveld refinement. Thereby, the crystallographic composition will not be determined reliably since the angular range is small and the number of counts low. On the other hand, however, the intensity of each individual peak as a function of time.
10.2. Outlook

could be obtained. Due to the large number of diffraction patterns, it is necessary to use a script which automatically runs the refinement process.

- By fitting the model for the Avrami equation 3.1 into the peak growth curvatures not only the times $t_0$, $\tau$, $t_{50\%}$, $\tau_e$ and $t_e$ were delivered, but also a lot of information within the fit parameters. The derived rate constant $k$ contains the nucleation rate and the growth rate. The parameter $n$ gives the type of nucleation rate which can either be zero, decreasing or increasing. Evaluating these will give insight into the nucleation and peak growth of the transformation products during decomposition of $\gamma$-UMo.

10.2.3 Complementing the TTT-Diagram for U8wt.-%Mo

The TTT-diagram developed throughout this work can be completed for a larger range in temperature and time. First of all, the transition into the high-temperature regime needs to be determined as suggested in Chapter 10.2.1. Moreover, in-situ annealing studies in order to obtain the beginning of phase decomposition for temperatures between 525 °C and $T_{\text{crit}}$, as well as for temperatures below 425 °C should be performed. Thereby, also the eutectoid temperature can be estimated. Due to the erroneous measurement at 475 °C, in-situ annealing investigation should be repeated. During this work, in-situ neutron diffraction, i.e. STRESS-SPEC, has been found to be the best solution for this kind of measurements. Pre-annealed samples can be used to determine behaviour of the phases at later times, as has been already been measured at 500 °C.

For further investigations, a denser grid of measurement points over a larger range in time needs to be prepared for crystallographic phase analysis. The equilibrium micro-structure can also be determined by preparing samples with very long annealing durations. As already discussed in Chapter 7, for less decomposed material high-energy X-ray diffraction should be preferred over neutron diffraction.

In conclusion, the studies performed throughout this thesis obtained a considerable amount of data. Thereby, the results revealed detailed characteristics in the transformation of $\gamma$-UMo and showed that adjustments to the TTT-diagram are necessary.
Part V

Appendix
## Chemical Analysis of the UMo-Ingot by AREVA-CERCA

### Chemical Analysis on 5 bricks along the ingot

Ingot 657 / Brick number from A01 to A20

<table>
<thead>
<tr>
<th>Element</th>
<th>DU-UMo-657-1</th>
<th>DU-UMo-657-5</th>
<th>DU-UMo-657-9</th>
<th>DU-UMo-657-13</th>
<th>DU-UMo-657-17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (%)</td>
<td>7.68 ± 0.08</td>
<td>7.82 ± 0.09</td>
<td>7.73 ± 0.18</td>
<td>7.89 ± 0.20</td>
<td>8.03 ± 0.14</td>
</tr>
<tr>
<td>V (%)</td>
<td>0.18 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>Al (µg/g)</td>
<td>800 ± 8</td>
<td>751 ± 8</td>
<td>716 ± 8</td>
<td>728 ± 8</td>
<td>700 ± 8</td>
</tr>
<tr>
<td>Fe (µg/g)</td>
<td>915 ± 9</td>
<td>870 ± 9</td>
<td>838 ± 10</td>
<td>857 ± 9</td>
<td>810 ± 9</td>
</tr>
<tr>
<td>Mn (µg/g)</td>
<td>15.9 ± 0.3</td>
<td>15.2 ± 0.3</td>
<td>15.1 ± 0.3</td>
<td>15.5 ± 0.3</td>
<td>14.6 ± 0.3</td>
</tr>
<tr>
<td>Cu (µg/g)</td>
<td>56.9 ± 0.8</td>
<td>60.5 ± 0.8</td>
<td>66.8 ± 0.8</td>
<td>66.9 ± 0.8</td>
<td>65.2 ± 0.8</td>
</tr>
<tr>
<td>Cr (µg/g)</td>
<td>67.7 ± 0.9</td>
<td>62.7 ± 0.8</td>
<td>68.3 ± 0.9</td>
<td>69.7 ± 0.8</td>
<td>65.6 ± 0.8</td>
</tr>
<tr>
<td>Zr (µg/g)</td>
<td>39.4 ± 1.2</td>
<td>32.1 ± 1.2</td>
<td>40.4 ± 1.2</td>
<td>39.7 ± 1.2</td>
<td>39.2 ± 1.2</td>
</tr>
<tr>
<td>W (µg/g)</td>
<td>104 ± 1</td>
<td>104 ± 1</td>
<td>152 ± 1</td>
<td>145 ± 1</td>
<td>141 ± 1</td>
</tr>
<tr>
<td>Ca (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Co (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cd (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cr (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mg (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Pb (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Ag (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Hg (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Li (µg/g)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
1. Manufacturing description

- The 40 UMo bricks were manufactured in using depleted U raw material.
- Two ingots were elaborated. As presented hereby 20 bricks were machined from each ingot (657 & 660). Mo% and isotopic composition were measured on the bricks identified in bold character in the following tables.

<table>
<thead>
<tr>
<th>Ingot 657 &amp; Brick reference</th>
<th>Ingot 660 &amp; Brick reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>Top</td>
</tr>
<tr>
<td>A19</td>
<td>C19</td>
</tr>
<tr>
<td>A18</td>
<td>C18</td>
</tr>
<tr>
<td>A17</td>
<td>C17</td>
</tr>
<tr>
<td>A16</td>
<td>C16</td>
</tr>
<tr>
<td>A15</td>
<td>C15</td>
</tr>
<tr>
<td>A14</td>
<td>C14</td>
</tr>
<tr>
<td>A13</td>
<td>C13</td>
</tr>
<tr>
<td>A12</td>
<td>C12</td>
</tr>
<tr>
<td>A11</td>
<td>C11</td>
</tr>
<tr>
<td>A10</td>
<td>C10</td>
</tr>
<tr>
<td>A9</td>
<td>C09</td>
</tr>
<tr>
<td>A8</td>
<td>C08</td>
</tr>
<tr>
<td>A7</td>
<td>C07</td>
</tr>
<tr>
<td>A6</td>
<td>C06</td>
</tr>
<tr>
<td>A5</td>
<td>C05</td>
</tr>
<tr>
<td>A4</td>
<td>C04</td>
</tr>
<tr>
<td>A3</td>
<td>C03</td>
</tr>
<tr>
<td>A2</td>
<td>C02</td>
</tr>
<tr>
<td>Bottom</td>
<td>Bottom</td>
</tr>
<tr>
<td>A1</td>
<td>C01</td>
</tr>
</tbody>
</table>

2. Inspections and results

- Chemical analysis of impurities: Not yet performed, in progress
- Appendix 1 Isotopic and Mo (w%) composition of the bricks: Conform
- Appendix 2: Ut and U235 mass per brick Ingot 657
- Appendix 3: Ut and U235 mass per brick Ingot 660
- Appendix 4: Holes position inspection sheet: Conform
- Appendix 5: Dimensional and Roughness inspection sheet: Conform

### Appendix 1 Isotopic and Mo (w%) composition of the bricks

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>U-232 (wt %)</th>
<th>U-234 (wt %)</th>
<th>U-235 (wt %)</th>
<th>U-238 (wt %)</th>
<th>Mo (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DU-8Mo-657-01</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.220</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-657-05</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.221</td>
<td>remaining</td>
<td>7.8</td>
</tr>
<tr>
<td>DU-8Mo-657-09</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.221</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-657-13</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-657-17</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.220</td>
<td>remaining</td>
<td>8.0</td>
</tr>
<tr>
<td>DU-8Mo-660-01</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.223</td>
<td>remaining</td>
<td>7.8</td>
</tr>
<tr>
<td>DU-8Mo-660-05</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.223</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-09</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-13</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-17</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.221</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-02</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.227</td>
<td>remaining</td>
<td>8.0</td>
</tr>
<tr>
<td>DU-8Mo-660-03</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-660-04</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.226</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-06</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.227</td>
<td>remaining</td>
<td>7.8</td>
</tr>
<tr>
<td>DU-8Mo-660-07</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.224</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-08</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.224</td>
<td>remaining</td>
<td>7.6</td>
</tr>
<tr>
<td>DU-8Mo-660-10</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.225</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-660-11</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.231</td>
<td>remaining</td>
<td>7.8</td>
</tr>
<tr>
<td>DU-8Mo-660-12</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.230</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-660-14</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.8</td>
</tr>
<tr>
<td>DU-8Mo-660-15</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.226</td>
<td>remaining</td>
<td>7.7</td>
</tr>
<tr>
<td>DU-8Mo-660-16</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.223</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-660-18</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.9</td>
</tr>
<tr>
<td>DU-8Mo-660-19</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.222</td>
<td>remaining</td>
<td>7.6</td>
</tr>
<tr>
<td>DU-8Mo-660-20</td>
<td>&lt; 0.0015</td>
<td>&lt; 0.0015</td>
<td>0.224</td>
<td>remaining</td>
<td>7.8</td>
</tr>
</tbody>
</table>

### Appendix 2: Ut and U235 mass per brick Ingot 657

<table>
<thead>
<tr>
<th>Bricks reference</th>
<th>Net mass</th>
<th>Wt% Mo</th>
<th>Ut mass</th>
<th>Ut %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.045</td>
<td>7.7</td>
<td>1.045</td>
<td>2.3</td>
</tr>
<tr>
<td>A2</td>
<td>1.041</td>
<td>7.7</td>
<td>1.041</td>
<td>2.2</td>
</tr>
<tr>
<td>A3</td>
<td>1.045</td>
<td>7.7</td>
<td>1.045</td>
<td>2.3</td>
</tr>
<tr>
<td>A4</td>
<td>1.051</td>
<td>7.7</td>
<td>1.051</td>
<td>2.3</td>
</tr>
<tr>
<td>A5</td>
<td>1.046</td>
<td>7.8</td>
<td>1.046</td>
<td>2.3</td>
</tr>
<tr>
<td>A6</td>
<td>1.040</td>
<td>7.8</td>
<td>1.040</td>
<td>2.3</td>
</tr>
<tr>
<td>A7</td>
<td>1.043</td>
<td>7.8</td>
<td>1.043</td>
<td>2.3</td>
</tr>
<tr>
<td>A8</td>
<td>1.045</td>
<td>7.8</td>
<td>1.045</td>
<td>2.3</td>
</tr>
<tr>
<td>A9</td>
<td>1.050</td>
<td>7.7</td>
<td>1.050</td>
<td>2.3</td>
</tr>
<tr>
<td>A10</td>
<td>1.052</td>
<td>7.7</td>
<td>1.052</td>
<td>2.3</td>
</tr>
<tr>
<td>A11</td>
<td>1.048</td>
<td>7.7</td>
<td>1.048</td>
<td>2.3</td>
</tr>
<tr>
<td>A12</td>
<td>1.048</td>
<td>7.7</td>
<td>1.048</td>
<td>2.3</td>
</tr>
<tr>
<td>A13</td>
<td>1.045</td>
<td>7.9</td>
<td>1.045</td>
<td>2.3</td>
</tr>
<tr>
<td>A14</td>
<td>1.046</td>
<td>7.9</td>
<td>1.046</td>
<td>2.3</td>
</tr>
<tr>
<td>A15</td>
<td>1.040</td>
<td>7.9</td>
<td>1.040</td>
<td>2.3</td>
</tr>
<tr>
<td>A16</td>
<td>1.040</td>
<td>7.9</td>
<td>1.040</td>
<td>2.3</td>
</tr>
<tr>
<td>A17</td>
<td>1.038</td>
<td>8.0</td>
<td>1.038</td>
<td>2.3</td>
</tr>
<tr>
<td>A18</td>
<td>1.044</td>
<td>8.0</td>
<td>1.044</td>
<td>2.3</td>
</tr>
<tr>
<td>A19</td>
<td>1.046</td>
<td>8.0</td>
<td>1.046</td>
<td>2.3</td>
</tr>
<tr>
<td>A20</td>
<td>1.049</td>
<td>8.0</td>
<td>1.049</td>
<td>2.3</td>
</tr>
<tr>
<td>Total</td>
<td>22675</td>
<td></td>
<td>20900</td>
<td>46.2</td>
</tr>
</tbody>
</table>
APPENDIX B

NIST Standard Certificates
and 62 reflections which were located in the angular region, 80 degrees to 130 degrees 2θ, wherein the effects of...a wavelength of 1.54060 nm [7]. The data collection temperature associated with a given hkl reflection were scanned sequentially. The angular widths of the scan ranges were approximately, 15 times the observed FWHM at half maximum. The step width was chosen to include at least 8 data points above the FWHM. The count time on each profile was inversely proportional to the peak intensity. The temperature of the specimen was recorded every 10th data point up to an uncertainty of ±0.01°C.

Peak positions were determined via the Fundamental Parameters Approach as implemented in TOPAS [8]. The refined parameters that were varied with the individual profiles included peak position, parameters of a linear background function, and the Kα profile fitting for Rietveld analyses of conventional X-ray powder data. The step width was chosen to include at least 8 data points above the FWHM and count times were also chosen so that the profile intensity had approximately the same X-ray count values. TOPAS was used to carry out the Fundamental Parameters Approach to profile fitting for a Rietveld analysis of the silicon profile data. The scale parameters and positions of the X-ray powder profile were constrained across the full pattern. These included the intensities and positions of the Kα and satellite components of the Cu Ka X-ray spectrum, the peak intensities of the silicon profiles to describe the content of particle size and strain index profile broadening, terms indicating the position and intensity of the "half" (θ2), the usual divergence angle of the diffracted beam, the sample displacement and linear attenuation terms, and the lattice parameter. Homogeneity of the silicon sample was judged in the context of variation in the lattice parameter and, the axial divergence angle of the incident beam was limited by a 1.9 degree Soller slit. The go niometer was equipped with an air-calibrating optical encoder resulting in an angular measurement uncertainty of approximately ±0.01° (0.00000092 nm).

The scale parameters and the lattice parameters were constrained over the entire 2θ range included the intensities and positions of the Kα and satellite components of the Cu Ka X-ray spectrum, and a parameter describing the content of two "top hats" (i.e., a blanking function) used to model the transmission function of the silicon sample. The data from each side of the direct beam were refined separately. Certified lattice data were determined from the R values, 0.235, 0.345, 0.545, 0.551.

REFERENCES

Users of this SRM should ensure that the certificate in possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-4776; fax (301) 979-4775; e-mail contact.srm@nist.gov; or via the Internet at http://srmd.nist.gov.
National Institute of Standards & Technology
Certificates
Standard Reference Material® 660a
Lanthanum Hexaboride Powder
Line Position and Line Shape Standard for Powder Diffraction

This Standard Reference Material (SRM) is intended for use as a standard for calibration of diffraction line positions and line shape parameters through a monitored procedure. A suite of SRM 660a consists of approximately 5 g of lanthanum hexaboride powder bounded under argon.

Material Description: The SRM material was prepared via a solid state process, Jeff and annealed. The powder was deagglomerated with a homogenizing operation at a rotation and profile, fine fractionated. The powder fraction was removed by passing through a 15 µm sieve using impinging as a supporting agent. The powder was then dried and heated under argon. An analysis of X-ray powder diffraction data indicated that the SRM material is homogeneous with respect to diffraction properties.

Certified Value and Uncertainty: The certified lattice parameter for a temperature of 22.5°C is 5.4659(-4) mm ± 0.0000005 mm.

The intervals defined by a value and its uncertainty in this certificate are 95% confidence intervals for the true value of the lattice constant in the absence of systematic errors [5].

Expiration of Certification: The certification of this SRM is to be utilized within the stated concentration, provided the SRM is stored and handled in accordance with the instructions given in this certificate (see Storage Section). This material degrades slowly with exposure to humidity. If excessive exposure is suspected, desiccation is required.

Storage: SRM 660a was handled under argon to prevent oxidation. When not in use, store the removed portion of this powder lightly capped in the original bottle or in a manner with similar or greater protection against oxidation.

This SRM was prepared and certified by J.P. Cleer of the NIST Composites Division, R.D. Dedenski, J.L. Stander, and L. Blasenbrey of the NIST American Physics Division, and R.W. Chaday of the University of Technology, Sydney, Australia.

The statistical analysis was provided by J.R. Fredrick of the NIST Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.R. Gittings and N.M. Traynor.

Stephanie M. Traynor, Chief
Composites Division

Gustofson, MD 20899
Certificate Issue Date: 13 September 2000
Nancy M. Traynor, Chief
Standard Reference Materials Program

SRM 660a

Page 2 of 4

The data collection temperature associated with each of the SrCa lattice parameter was within ±8 degrees, four degrees each from the two profiles. The temperature extremes used were those that defined the Sr and Ca ions, from each of such reflections recorded during the X-ray data collection. The data collection of SRM 660a (certified in this certificate), indicated that the instrumental effect of the room temperature due to local temperature fluctuation was negligibly small.

Certain commercial equipment, instruments, or materials are identified in this certificate (or report) to adequately specify some test parameters or methodology. Such identification does not imply that the materials or equipment identified are necessarily the best available for the purpose specified.

SRM 660a

Page 3 of 4

Figure 1. Typical Particle Size Distribution as Determined by Laser Scattering

REFERENCES


APPENDIX C

Tables

C.1 Data on Phase Decomposition Measurements During In-Situ Annealing

Table C.1: Fit parameter for the Avrami equation along with the results for \( \tau \) and \( \tau_e \); also given: adjusted \( R^2 \), point of inflection \( IP \) and the slope at the point of inflection \( IPs \) – \( \alpha \)-peak growths at 525 °C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \alpha_{110} )</th>
<th>( \alpha_{111} )</th>
<th>( \alpha_{021/002} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B )</td>
<td>1751.08 ± 78.43</td>
<td>4614.9 ± 114.02</td>
<td>13476.21 ± 133.77</td>
</tr>
<tr>
<td>( A )</td>
<td>15681.96 ± 616.66</td>
<td>16044.54 ± 1594.87</td>
<td>34226.61 ± 1405.39</td>
</tr>
<tr>
<td>( k )</td>
<td>((0.290441 ± 1.00814) \cdot 10^{-b})</td>
<td>((0.531208 ± 3.49286) \cdot 10^{-7})</td>
<td>((1.05584 ± 3.0882) \cdot 10^{1})</td>
</tr>
<tr>
<td>( t_0 )</td>
<td>15.4712 ± 24.5624</td>
<td>0 ± 46.0243</td>
<td>0 ± 21.8822</td>
</tr>
<tr>
<td>( n )</td>
<td>2.86519 ± 0.58126</td>
<td>3.1308 ± 1.07244</td>
<td>2.9945 ± 0.47719</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9984</td>
<td>0.9977</td>
<td>0.9993</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Results</th>
<th>( \tau )</th>
<th>( \tau_e )</th>
<th>( IP )</th>
<th>( IPs )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{110} )</td>
<td>99.1112 ± 6.95016</td>
<td>101.053 ± 14.7822</td>
<td>180.074/9254.38</td>
<td>92.6763</td>
</tr>
<tr>
<td>( \alpha_{111} )</td>
<td>101.053 ± 14.7822</td>
<td>273.74 ± 10.2224</td>
<td>186.306/12535.8</td>
<td>92.9109</td>
</tr>
<tr>
<td>( \alpha_{021/002} )</td>
<td>98.019 ± 6.50825</td>
<td>280.085 ± 4.794</td>
<td>186.552/30119.5</td>
<td>187.99</td>
</tr>
</tbody>
</table>
### Table C.2: Fit parameter for the Avrami equation along with the results for $\tau$ and $\tau_e$; also given: adjusted $R^2$, point of inflection $IP$ and the slope at the point of inflection $IPs$ - $\alpha$-peak growths at 500 °C

<table>
<thead>
<tr>
<th>Fit Parameter</th>
<th>$\alpha_{110}$</th>
<th>$\alpha_{111}$</th>
<th>$\alpha_{021/002}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>573.47 ± 75.75</td>
<td>380.83 ± 73.33</td>
<td>8898.27 ± 188.14</td>
</tr>
<tr>
<td>$A$</td>
<td>18881.39 ± 320.03</td>
<td>18152.28 ± 315.46</td>
<td>42749.04 ± 882.67</td>
</tr>
<tr>
<td>$k$</td>
<td>$(0.67721 ± 1.38535) \cdot 10^{-7}$</td>
<td>$(0.72015 ± 1.5637) \cdot 10^{-7}$</td>
<td>$(0.78256 ± 1.84422) \cdot 10^{-7}$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>24.6049 ± 14.056</td>
<td>36.7809 ± 14.7499</td>
<td>15.057 ± 17.7875</td>
</tr>
<tr>
<td>$n$</td>
<td>3.01855 ± 0.33756</td>
<td>3.02748 ± 0.36074</td>
<td>2.9717 ± 0.38489</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9982</td>
<td>0.9980</td>
<td>0.9981</td>
</tr>
<tr>
<td>Results</td>
<td>$\tau$ 134.311 ± 6.15001</td>
<td>142.881 ± 6.28544</td>
<td>127.216 ± 7.15013</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>335.016 ± 2.60335</td>
<td>335.909 ± 2.45692</td>
<td>338.68 ± 2.71055</td>
</tr>
<tr>
<td>$IP$</td>
<td>232.181/9780.66</td>
<td>237.105/9241.57</td>
<td>229.759/90628.1</td>
</tr>
<tr>
<td>$IPs$</td>
<td>94.0397</td>
<td>92.1492</td>
<td>202.157</td>
</tr>
</tbody>
</table>

### Table C.3: Fit parameter for the Avrami equation along with the results for $\tau$ and $\tau_e$; also given: adjusted $R^2$, point of inflection $IP$ and the slope at the point of inflection $IPs$ - $\alpha$-peak growths at 475 °C

<table>
<thead>
<tr>
<th>Fit Parameter</th>
<th>$\alpha_{110}$</th>
<th>$\alpha_{111}$</th>
<th>$\alpha_{021/002}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>808.15 ± 39.93</td>
<td>518.93 ± 38.09</td>
<td>6171.16 ± 78.88</td>
</tr>
<tr>
<td>$A$</td>
<td>30240.88 ± 3222.37</td>
<td>64178.71 ± 57817.52</td>
<td>53450.44 ± 5569.19</td>
</tr>
<tr>
<td>$k$</td>
<td>$(0.598488 ± 2.33143) \cdot 10^{-9}$</td>
<td>$(1.8046 ± 4.60911) \cdot 10^{-9}$</td>
<td>$(1.9386 ± 7.9148) \cdot 10^{-10}$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>47.0227 ± 52.3855</td>
<td>31.3105 ± 50.2011</td>
<td>0 ± 57.548</td>
</tr>
<tr>
<td>$n$</td>
<td>3.31955 ± 0.55838</td>
<td>2.94891 ± 0.48199</td>
<td>3.46382 ± 0.56356</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9978</td>
<td>0.9977</td>
<td>0.9984</td>
</tr>
<tr>
<td>Results</td>
<td>$\tau$ 350.806 ± 24.4646</td>
<td>447.787 ± 103.267</td>
<td>334.304 ± 31.4683</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>817.735 ± 35.3535</td>
<td>1244.43 ± 446.188</td>
<td>811.369 ± 36.0183</td>
</tr>
<tr>
<td>$IP$</td>
<td>585.582/16013.5</td>
<td>833.051/31556.4</td>
<td>577.128/32785.2</td>
</tr>
<tr>
<td>$IPs$</td>
<td>64.7655</td>
<td>80.5614</td>
<td>112.04</td>
</tr>
</tbody>
</table>

### Table C.4: Fit parameter for the Avrami equation along with the results for $\tau$ and $\tau_e$; also given: adjusted $R^2$, point of inflection $IP$ and the slope at the point of inflection $IPs$ - $\alpha$-peak growths at 450 °C

<table>
<thead>
<tr>
<th>Fit Parameter</th>
<th>$\alpha_{110}$</th>
<th>$\alpha_{111}$</th>
<th>$\alpha_{021/002}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>115.56 ± 31.38</td>
<td>405.00 ± 36.61</td>
<td>5295.35 ± 84.96</td>
</tr>
<tr>
<td>$A$</td>
<td>21467.88 ± 254.67</td>
<td>20865.44 ± 257.34</td>
<td>48159.47 ± 664.59</td>
</tr>
<tr>
<td>$k$</td>
<td>$(3.15082 ± 3.62138) \cdot 10^{-8}$</td>
<td>$(3.17074 ± 3.95584) \cdot 10^{-8}$</td>
<td>$(3.48981 ± 4.71016) \cdot 10^{-8}$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>87.1453 ± 10.5434</td>
<td>83.2291 ± 11.2485</td>
<td>78.5093 ± 12.6595</td>
</tr>
<tr>
<td>$n$</td>
<td>2.98615 ± 0.1792</td>
<td>2.98926 ± 0.19524</td>
<td>2.96198 ± 0.21</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9995</td>
<td>0.9993</td>
<td>0.9993</td>
</tr>
<tr>
<td>Results</td>
<td>$\tau$ 235.887 ± 4.70033</td>
<td>230.927 ± 5.13223</td>
<td>227.871 ± 5.59641</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>513.642 ± 1.62192</td>
<td>506.187 ± 1.96522</td>
<td>511.155 ± 2.4046</td>
</tr>
<tr>
<td>$IP$</td>
<td>370.817/10544.4</td>
<td>364.694/10544.9</td>
<td>365.089/28622.9</td>
</tr>
<tr>
<td>$IPs$</td>
<td>77.2906</td>
<td>75.8027</td>
<td>170.004</td>
</tr>
</tbody>
</table>
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Reactor cross section and fuel element of the Frm II</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>(a) core cross section</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>(b) fuel element</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Three Allotropes in which the pure uranium metal occur</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(a) α-phase of uranium</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(b) β-phase of uranium</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(c) γ-phase of uranium</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Damage in fine grained highly textured α-uranium</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(a) Damage due to irradiation</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>(b) Damage due to thermal cycling</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>Effect of zirconium additions on the stability of cast uranium irradiated</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>to 0.6at.-% burn-up [16]</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>Relationship between γ-phase stability and uranium density for the alloys</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>UNb, UNbZr and UMo</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>UMo phase diagram [7, 19]</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>Intermetallic compound U₂Mo</td>
<td>14</td>
</tr>
<tr>
<td>3.1</td>
<td>Comparison between a growth curve and a corresponding TTT-diagram</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>(a) Growth curve for a product region [30]</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>(b) TTT-diagram (top) and growth curve (down) [35]</td>
<td>18</td>
</tr>
<tr>
<td>3.2</td>
<td>Eutectoidal transformation of a high temperature γ-phase into two phases</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>α and β</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Equilibrium diagram of an exemplary alloy [31]</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>(b) TTT-diagram for the decomposition of the γ-phase in an exemplary alloy</td>
<td>19</td>
</tr>
<tr>
<td>3.3</td>
<td>TTT-diagram for U8wt.-%Mo</td>
<td>21</td>
</tr>
<tr>
<td>4.1</td>
<td>Diffraction according to Bragg’s law</td>
<td>24</td>
</tr>
<tr>
<td>4.2</td>
<td>Geometries used for powder diffraction</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>(a) Bragg-Brentano-Geometry</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>(b) Debye-Scherrer-Geometry</td>
<td>25</td>
</tr>
<tr>
<td>5.1</td>
<td>Sample preparation equipment in the radionuclide laboratory</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>(a) Electric arc furnace</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>(b) Diamond wire saw</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>(c) HT furnace</td>
<td>33</td>
</tr>
<tr>
<td>5.2</td>
<td>TTT-diagram for an U8wt.-%Mo alloy [38] where all measured samples are</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>listed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Stages of sample preparation</td>
<td>36</td>
</tr>
</tbody>
</table>
List of Figures

6.1 Microscope images of sample A-425C6h ........................................... 37
(a) Optical microscope image ......................................................... 37
(b) Scanning electron microscope image ......................................... 37

6.2 Parasitic scattering effect due to the aperture system at the HEMS on the example of sample A-475C16h ...................................................... 40
(a) Detector image of the measurement; parasitic scattering effect is highlighted in red ......................................................... 40
(b) Rietveld refinement with enlarged detail which shows the peaks caused by the aperture; the effect is not considered in the fit ......................... 40

6.3 Experimental set-up at SPODI .................................................... 41
(a) Schematic representation of SPODI [1] ........................................ 41
(b) Set-up of SPODI at the FRM II .................................................. 41

6.4 Rietveld refinements of the NIST Si-640c standards at SPODI (a) and STRESS-SPEC (b), respectively ............................................... 41
(a) SPODI ......................................................................................... 41
(b) STRESS-SPEC .......................................................................... 41

6.5 Detector image collected at SPODI on the example of A-initial ............... 42

6.6 Detector images obtained at STRESS-SPEC ...................................... 43
(a) Detector image of an empty vanadium container inside the experimental set-up at STRESS-SPEC ............................................... 43
(b) Corrected detector image of sample A-450C7h at the end of annealing ... 43

6.7 Experimental set-up at STRESS-SPEC ............................................ 44
(a) High temperature vacuum furnace installed at STRESS-SPEC .......... 44
(b) Specimen carrier ........................................................................... 44

7.1 Exemplary diffraction pattern of a decomposed U8wt.-%Mo sample with the phase description drawn in .......................................................... 48

7.2 Refinement of the diffraction pattern of the highly homogeneous γ-UMo collected at SPODI ............................................................... 49
(a) Refinement of the reference γ-UMo phase ..................................... 49
(b) Detector image of the γ-phase at SPODI ........................................ 49

7.3 Rietveld Refinement at 475 °C ....................................................... 52
(a) A-475C3h: 3h at 475 °C; high-energy X-rays .................................. 52
(b) A-475C6h: 6h at 475 °C; neutrons ............................................... 52
(c) A-475C16h: 16h at 475 °C; high-energy X-rays .............................. 52
(d) A-475C24h: 24h at 475 °C; neutrons ........................................... 52
(e) A-475C48h: 48h at 475 °C; neutrons ........................................... 52

7.4 Rietveld Refinement at 500 °C ....................................................... 55
(a) A-500C3h: 3h at 500 °C; neutrons ............................................... 55
(b) A-500C6h: 6h at 500 °C; high-energy X-rays .................................. 55
(c) A-500C16h: 16h at 500 °C; high-energy X-rays .............................. 55
(d) A-500C48h: 24h at 500 °C; neutrons ........................................... 55

7.5 Rietveld Refinement at 450 °C ....................................................... 58
(a) A-450C3h: 3h at 450 °C; neutrons ............................................... 58
(b) A-450C6h: 6h at 450 °C; high-energy X-rays .................................. 58
(c) A-450C16h: 16h at 450 °C; high-energy X-rays .............................. 58
(d) A-450C48h: 24h at 450 °C; neutrons ........................................... 58
7.6 Rietveld Refinement at 450 °C
(a) A-425C3h: 3h at 425 °C; neutrons
(b) A-425C6h: 6h at 425 °C; high-energy X-rays
(c) A-425C24h: 24h at 425 °C; high-energy X-rays

7.7 Rietveld Refinement at 400 °C
(a) A-400C24h: 24h at 400 °C; neutrons
(b) A-400C48h: 48h at 400 °C; neutrons

8.2 Waterfall chart of the γ-UMo phase decomposition as a function of the annealing time at 500 °C
8.3 Growth of the α-peaks during annealing at 500 °C as a function of the annealing time
(a) Growth of the α110-peak
(b) Growth of the α111-peak
(c) Growth of the α021/002-peaks
(d) Further growth of the α110-peak

8.4 Waterfall chart of the γ-UMo phase decomposition as a function of the annealing time at 525 °C
8.5 Growth of the α-peaks during annealing at 525 °C as a function of the annealing time
(a) Growth of the α110-peak
(b) Growth of the α111-peak
(c) Growth of the α021/002-peaks

8.6 Waterfall chart of the γ-UMo phase decomposition as a function of the annealing time at 475 °C
8.7 Growth of the α-peaks during annealing at 475 °C as a function of the annealing time
(a) Growth of the α110-peak
(b) Growth of the α111-peak
(c) Growth of the α021/002-peaks

8.8 Waterfall chart of the γ-UMo phase decomposition as a function of the annealing time at 450 °C
8.9 Growth of the α-peaks during annealing at 450 °C as a function of the annealing time
(a) Growth of the α110-peak
(b) Growth of the α111-peak
(c) Growth of the α021/002-peaks

8.10 Diffraction patterns and growth of the α-peaks during annealing at 425 °C as a function of the annealing time
(a) Diffraction patterns at the beginning, after 5h and after 10h of annealing at 425 °C
(b) Growth of the α110-peak
(c) Growth of the α111-peak

8.11 Transition into the high-temperature γ-phase
(a) Diffraction patterns along the transition process
(b) α-peaks shrinking as a function of temperature and time
List of Figures

9.2 Isothermal transformation curves describing the region where the latest end of $U_2\text{Mo}$ fast growth in U8wt.-%Mo is ............................................................ 83
List of Tables

2.1 Crystallographic parameters of the different phases in uranium and uranium-molybdenum .......................................................... 7

5.1 List of U8wt.-%Mo samples .......................................................... 32

7.1 Lattice constants, crystallographic composition and final agreement factors of the Rietveld refinement of the U8wt.-%Mo reference sample .......................................................... 50

7.2 Crystallographic composition of U8wt.-%Mo for isothermal studies at 475 °C .......................................................... 51

7.3 Lattice constants of the particular phases for the isothermal studies at 475 °C .......................................................... 51

7.4 Agreement factors obtained by Rietveld refinement for the isothermal studies at 475 °C .......................................................... 53

7.5 Crystallographic composition of U8wt.-%Mo for isothermal studies at 500 °C .......................................................... 54

7.6 Lattice constants of the particular phases for the isothermal studies at 500 °C .......................................................... 55

7.7 Agreement factors obtained by Rietveld refinement for the isothermal studies at 500 °C .......................................................... 56

7.8 Crystallographic composition of U8wt.-%Mo for isothermal studies at 450 °C .......................................................... 57

7.9 Lattice constants of the particular phases for the isothermal studies at 450 °C .......................................................... 57

7.10 Agreement factors obtained by Rietveld refinement for the isothermal studies at 450 °C .......................................................... 57

7.11 Crystallographic composition of U8wt.-%Mo for isothermal studies at 425 °C .......................................................... 59

7.12 Lattice constants of the particular phases for the isothermal studies at 425 °C .......................................................... 60

7.13 Agreement factors obtained by Rietveld refinement for the isothermal studies at 425 °C .......................................................... 61

7.14 Crystallographic composition of U8wt.-%Mo for isothermal studies at 400 °C .......................................................... 62

7.15 Lattice constants of the particular phases for the isothermal studies at 400 °C .......................................................... 62

7.16 Agreement factors obtained by Rietveld refinement for the isothermal studies at 400 °C .......................................................... 62

C.1 Fit parameter for the Avrami equation along with the results for \( \tau \) and \( \tau_e - \alpha \)-peak growths at 525 °C .......................................................... ix

C.2 Fit parameter for the Avrami equation along with the results for \( \tau \) and \( \tau_e - \alpha \)-peak growths at 500 °C .......................................................... x

C.3 Fit parameter for the Avrami equation along with the results for \( \tau \) and \( \tau_e - \alpha \)-peak growths at 475 °C .......................................................... x

C.4 Fit parameter for the Avrami equation along with the results for \( \tau \) and \( \tau_e - \alpha \)-peak growths at 450 °C .......................................................... x
Bibliography


Isothermal Transformation Kinetics in Uranium Molybdenum Alloys

Indexes


Acknowledgement

At this point, I would like to thank a large number of people who contributed to this thesis and supported me throughout this work.

First of all my supervisor Prof. Dr. Winfried Petry for giving me the opportunity to do my master thesis on such an interesting project.

PD Dr. Christoph Morkel for his interesting lectures on reactor physics which led me to this topic, and for accepting to be the second assessor of my thesis.

My colleagues at the FRM II HEU-MEU group for the excellent working climate and atmosphere: Bruno Baumeister, Dr. Harald Breitkreutz, Tobias Chemnitz, Hsin-Yin Chiang, Matthias Dodenhöft, Alexandra Egle, Dr. Rainer Großmann, Tobias Hollmer, Tanja Huber, Dr. Rainer Jungwirth, Christian Reiter, Dr. Anton Röhrmoser, Rupert Schauer, Robert Schenk, Christian Steyer and Tobias Zweifel.

The beamline scientists at Spodi, Dr. Markus Hözel and Dr. Anatoliy Senyshyn, and Stress-Spec, Dr. Michael Hofmann and Dr. Weimin Gan, for their great support during my beam times at the FRM II. Moreover, the beamline scientists Dr. Uta Rütt and Olof Gutowski from the HEMS at the DESY.

Prof. Dr. Wolfgang Schmahl and PD Dr. Soyhun Park from the Fakultät für Geowissenschaften - Department für Geo- und Umweltwissenschaften at the Ludwigs-Maximilians-Universität in Munich for the permission to use their XRD set-up and their support.

Dr. Jürgen Peters and Markus Göhr from the Heinz Maier-Leibnitz Zentrum MLZ Sample Environment for their support during the beam time at Stress-Spec.

Dr. Harald Breitkreutz and Tobias Zweifel for the time consuming discussions and for proofreading.

Very special thanks to Dr. Rainer Jungwirth for his great supervision and energetic support throughout my thesis, especially during our beam times.

Last but not least my parents Doris and Jürgen Säubert for their support and for giving me the opportunity to go to university; and my brother Christof Säubert for his support in almost everything.
Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbständig und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Alle Stellen, die wörtlich oder sinngemäß aus Veröffentlichungen entnommen sind, wurden als solche kenntlich gemacht.

Die Arbeit wurde in gleicher oder ähnlicher Form keiner anderen Prüfungsordnung vorgelegt.

München, den 30. September 2013

Steffen Säubert
Revisions


30.09.2013:
• Officially submitted version

23.10.2013:
• Corrected Figure 7.1: label was not fully visible
• Corrected Figure 8.3d: $\alpha(1 \ 1 \ 0) \rightarrow \alpha_{110}$ in the legend
• Corrected Equation 8.1: added a missing bracket