Hydrogen absorption in uranium-based alloys with cubic $\gamma$-U structure

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Abstract

UH$_3$-type hydrides were formed by hydrogenation of splat-cooled U-based alloys upon applying high H$_2$ pressures (>2.5 bar). Hydrogenation of U$_{1-x}$Mo$_x$ alloys (with $x \geq 0.12$ (12 at.% Mo) containing the cubic $\gamma$-U phase leads to a formation of nanocrystalline $\beta$-UH$_3$, why those of U$_{1-x}$Zr$_x$ alloys (with $x \geq 15$ at.% Zr) implies a pure $\alpha$-UH$_3$. The Curie temperature of hydride (UH$_3$)$_{0.85}$Mo$_{0.15}$ reaches 200 K; it may be the first U-based ferromagnet with such high $T_C$. The results reflect the dominant U--H interaction.

Keywords: nanocrystalline $\beta$-UH$_3$, pure $\alpha$-UH$_3$, superconductivity, ferromagnetism

Classification numbers: 1.00, 4.00

1. Introduction

Metallic uranium consisting of the orthorhombic $\alpha$-U phase (at and below the ambient temperature) strongly reacts to hydrogen even at very low pressures (mbar), forming uranium-trihydride (UH$_3$) which is a nasty pyrophoric powder which self-ignites in air [1]. Thus UH$_3$ is considered as a hazard during the storage of uranium metal. On the other hand, due to its high absorption rate, uranium has been used particularly as a storage medium for tritium in the nuclear industry [2]. UH$_3$ itself can be used e.g. as an intermediate in the synthesis of uranium compounds [1].

Beside of the stable orthorhombic $\alpha$-U phase, two more phases of uranium exist at high temperatures: the tetragonal $\beta$-U and cubic $\gamma$-U phase formed respectively in the temperature range of 940–1045 K and 1045–1405 K [1]. The cubic $\gamma$-U phase can be retained to low temperatures by alloying with transition metals. Such alloys with the cubic $\gamma$-U phase have a higher resistance to corrosion and better accommodate radiation damage (than those with $\alpha$-U phase) and thus they are considered as better materials for nuclear fuels [3].

We have recently succeeded with stabilization of the cubic $\gamma$-U phase by alloying with Mo, Zr, Pt, Nb, Ti, Ru in a combination with ultrafast cooling. We have thoroughly investigated the electromagnetic properties of these materials, since they exhibit the superconducting ground state with critical temperature $T_c$ below 2.2 K. Besides, we are interested in underlining the hydrogen absorption ability in these splat-cooled alloys as well as hydrogen influence on the electromagnetic properties. It is known that for the nearest U--U distance, $d_{\text{U-U}} < 3.40$ Å, the U-based compounds have a paramagnetic ground state and are often superconducting at low temperatures, while for $d_{\text{U-U}} > 3.60$ Å they are usually magnetic, accordingly to the Hill limit [4]. Thus we expect that the increase of $d_{\text{U-U}}$ upon hydrogenation would lead to an appearance of the uranium magnetism in the hydrides formed from those $\gamma$-U phase alloys.

UH$_3$ is the only binary uranium hydride. However, it has two crystal structures denoted as $\alpha$-UH$_3$ and $\beta$-UH$_3$ which are both cubic with a similar crystal densities (11.12 g cm$^{-3}$ and 10.92 g cm$^{-3}$ respectively). $\alpha$-UH$_3$ is a metastable phase formed at relatively low temperatures which slowly converts to the stable $\beta$-UH$_3$ phase at high-temperatures. In $\alpha$-UH$_3$, U atoms (in 2$a$ sites) form a body-centered cubic (bcc) lattice ($a = 4.16$ Å) and H atoms locate on the faces of the cube. Each U atom is surrounded by 12 hydrogen atoms formed a slightly distorted icosahedrons (with a uranium--hydrogen...
spacing \( d_{\text{U-H}} \) of 2.32 Å. The shortest U–U distance in \( \alpha\)-UH\(_3\) is about 3.60 Å, much larger than that in \( \alpha\)-U: \( d_{\text{U-U}} = 2.80 \) Å). \( \beta\)-UH\(_3\) has a much larger unit cell (\( a = 6.64 \) Å) containing two different uranium sites: 2 uranium atoms (U1) located at the \( bcc\) sites of the cubic structure (as that of \( \alpha\)-UH\(_3\) (2\( a \) positions)) and other 6 uranium atoms (U2) (formed 3 pairs) on the faces of the cube (the 6\( c \) position; i.e. at the positions of hydrogen in \( \alpha\)-UH\(_3\)). The hydrogen-isocahedrons around U1 atoms have the same symmetry as that for \( \alpha\)-UH\(_3\), while those around U2 atoms (with \( d_{\text{U-H}} = 2.30 \) Å) are arranged less symmetrically. With respect to the hydrogen atoms, they are located at the center of distorted tetrahedra formed by the uranium atoms. The shortest U–U distance in \( \beta\)-UH\(_3\) (between U2 atoms in 6\( c \) position) is about 3.31 Å, i.e. much shorter than that in \( \alpha\)-UH\(_3\) (see Table 1). For a most recent review of UH\(_3\), see the introduction in [5].

Both \( \alpha\)-UH\(_3\) and \( \beta\)-UH\(_3\) are ferromagnets with Curie temperature \( (T_C)\) in the range of 165–180 K and the uranium magnetic moment of about \( \mu_U = 0.9 \) \( \mu_B/U\) [6]. We remind here that \( \alpha\)-U is a weak Pauli paramagnetic. The crystal structure expansion by hydrogen in UH\(_3\) leads to the formation of U magnetic moment. It is explained in the context of a reduction in the overlap of the 5\( f \) wave functions between nearest U neighbors implying a reduction of the 5\( f \) bandwidth and an increase the density of state at the Fermi level \( N(E_F)\). Indeed, the Sommerfeld coefficient of the electronic specific heat was found to be \( \gamma_e = 29 \) mJ K\(^{-2}\) mol\(^{-1}\) for \( \beta\)-UH\(_3\) [7], almost 3 times larger than that in \( \alpha\)-U (\( \gamma_e = 11 \) mJ K\(^{-2}\) mol\(^{-1}\)) [8].

Our investigations revealed that all splat-cooled \( \gamma\)-U alloys (e.g. U-15 at.\% Mo) are very stable in the ambient hydrogen atmosphere: no measurable hydrogen absorption at atmospheric pressure (1 bar H\(_2\)) was found. These alloys can absorb hydrogen but only upon applying high pressures higher than 2.5 bars. The formed hydrides (UH\(_3\))\(_{1-x}\)T\(_x\) are ferromagnets with enhanced Curie temperature around 180–200 K. The crucial point of our study is that using Zr alloying we succeeded to synthesize the \( \alpha\)-UH\(_3\) phase (without a transformation to \( \beta\)-UH\(_3\)) as a pure phase, while using Mo alloying lead to formation of the nanocrystalline \( \beta\)-UH\(_3\).

In this work we summarize our investigations of the crystal structure and magnetic properties of the two different UH\(_3\) phases in the hydrides formed from splat-cooled \( \gamma\)-U alloys. In order to get a deeper understanding of the properties of the hydrides, we investigated also carefully the properties of their metallic precursors (i.e. the \( \gamma\)-U alloys).

### 2. Experimental

U-T alloys (T = Mo, Zr, Pt, Nb, Ti, Ru) with low T concentrations (up to 30 at.\%) were prepared by arc-melting in argon atmosphere. The splat-cooled sample was prepared from the alloy-ingot by splat-cooling technique. The splat-samples are thin foils (with a thickness of 100–200 \( \mu m \)) and a disc shape (with a diameter of 15–20 mm). More details of preparation of the splats have been reported earlier [8, 9].

We notice that by means of splat-cooling technique with the cooling rate in the range of 10\(^6\) K s\(^{-1}\), we are able to retain the cubic \( \gamma\)-U phase to the ambient temperature with a reduced necessary amount of the alloying element. For instance, the cubic \( \gamma\)-U phase (with a small tetragonal distortion called \( \gamma\)-U) without any trace of orthorhombic \( \alpha\)-U phase was obtained in the splat-cooled U-11 at.\% Mo alloy (i.e. U alloyed with 11 at.\% Mo) [8], i.e. several percent of Mo lower than that obtained by a standard furnace cooling (in U-16.5 at.\% Mo) [10]. Besides, using the splat cooling we can increase the Pt solubility in \( \gamma\)-U phase up to at least 15 at.\% Pt [11] and stabilize this phase (in U-15 at.\% Pt) down to room temperature, while the Pt solubility in standard conditions is reported to be only up to 5 at.\%. Another advantage is that the thin-foil splats can be used directly for the XRD measurements (the bulk alloys are hard and cannot be crushed into powder). It is also easy for cutting the foils to get proper size samples for other measurements.

For the hydrogenation, the samples were placed in an alumina crucible into a reactor, which could be pressurized to 150 bar of H\(_2\) gas. The reactor was first evacuated down to 10\(^{-6}\) mbar and then H\(_2\) gas was introduced. We found that minimum H\(_2\) pressure for the hydride formation of the U-T

### Table 1. Summary of crystal structure (at 300 K) and electro-magnetic properties of selected U-T alloys (T = Mo, Zr, Pt, Nb, Ti, Ru).

| Alloy          | \( a (\text{Å}) \) | \( d_{\text{U-U}} (\text{Å}) \) | \( T_C (\text{K}) \) | \( \mu_B \mu_H (0) (\text{T}) \) | \( \gamma_e (\text{mJ K}^{-2} \text{U}^{-1}) \) | \( T_C (\text{K}) \) | \( M_s (\mu_B/U) \) |
|---------------|-------------------|-------------------------------|---------------------|---------------------------------|---------------------------------|---------------------|---------------------|
| \( \alpha\)-U  | 2.80              | 2.06                          | 0.3                 | 11                              |                                 |                     |                     |
| \( \alpha\)\(_{0.65}\)Mo\(_{0.15}\) \( (\gamma\)-U\) | 3.44              | 3.00                          | 2.11                | 6.7                             | 18.8                            |                     |                     |
| \( \alpha\)\(_{0.65}\)Zr\(_{0.15}\) \( (\alpha\)+\( \gamma\)-U\) | 3.54              | 3.06                          | —                   | —                               | —                               |                     |                     |
| \( \alpha\)\(_{0.70}\)Zr\(_{0.30}\) \( (\gamma\)-U\) | 3.54              | 3.07                          | 0.8                 | 2.2                             | 16.9                            |                     |                     |
| \( \alpha\)-UH\(_3\) | 4.16              | 3.60                          | —                   | —                               | —                               |                     |                     |
| \( \beta\)-UH\(_3\) | 6.64              | 3.31(6c)                      | —                   | 28.5\(^{a}\)                    | 165–170\(^{a}\)                 | 0.9\(^{a}\)         |                     |
| (UH\(_3\))\(_{0.85}\)Mo\(_{0.15}\) \( (\beta\)-UH\(_3\)\) | 6.65              | 3.33                          | —                   | 34.4                            | 200                             | 1.15                |                     |
| (UH\(_3\))\(_{0.85}\)Zr\(_{0.15}\) \( (\alpha\)-UH\(_3\)\) | 4.14              | 3.58                          | —                   | —32                             | 185                             | 0.90                |                     |
| (UH\(_3\))\(_{0.85}\)Zr\(_{0.30}\) \( (\alpha\)-UH\(_3\)\) | 4.14              | 3.58                          | —                   | 34                             | 170                             | 0.85                |                     |
splits is about 2.5 bar, irrespective of composition. Higher pressures (up to 100 bar) can only fasten the process, but the absorbed H amount remains the same. The desorption in a closed evacuated volume was performed to determine the total H concentration. The total amount of H₂ released corresponds approximately to 3 H atoms per 1 U atom, suggesting that uranium with hydrogen form well-defined structure units, which are only weakly affected by alloying atoms.

Throughout our work, the T-content is given in the atomic percent (at.%). Several types of sample notation have been used. Namely, the alloy with 15 at.% Mo is marked as U-15at.% Mo, or U₀.₈₅M₀₀₁₅ or UM₀₁₈. The hydride formed from hydrogenation of U₀.₈₅M₀₀₁₅ is denoted as (UH)₀.₈₅M₀₀₁₅ or UH₃M₀₀₁₈.

For the splits, we use the sample pieces with proper sizes required for different measurements. For the hydrides, we use the powder samples.

The sample characterizations and investigations are carried out by means of standard techniques such as x-ray diffraction, closed cycle refrigerator system (CCR), quantum design physical properties measurement system (PPMS) and magnetic properties measurement system (MPMS) in the temperature range of 0.3–300 K and in magnetic fields up to 14 T, described earlier [8, 9].

Phase purity analysis, microstructure study have been performed on several splits by means of x-ray energy dispersive microanalysis (EDX) using the scanning electron microscope (SEM), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM). The splits show in most cases a homogeneous distribution of the alloying elements with concentrations corresponding the nominal ones.

3. Superconductivity of the splat-cooled U-T alloys containing the γ-U phase

In general, increasing the T alloying content (T = Mo, Zr, Pt, Nb) leads to a rapid suppression of numerous α-U peaks and an enhancement of γ-U peaks due to the development of the γ-U phase. Our detail investigations performed on U-Mo system showed that a pure cubic γ-U phase with an ideal A2 structure could be obtained only for U₀.₈₅M₀₀₁₅ revealed by single and sharp γ-U peaks without any diffusion in the XRD pattern. EBSD analysis also proved a homogenous γ-U phase [8, 9]. For other element alloying, we have performed the investigations for the T-content in a similar range of 0–15 at.% focusing on the alloys with the same 15 at.% T content. The XRD pattern of U₀.₈₅P₀₀₁₅ revealed γ-U type structure with a small trace of α-U phase [11]. For the U₀.₈₅Nb₀₀₁₅ alloy, the splitting of the γ-reflections into doublets indicating a stabilization of the γ-U phase, i.e. a cubic structure with a small tetragonal distortion [12]. Unlike other T alloying, the dominant α(1 1 0) and α(1 1 1) reflections still persist for U₀.₈₅Z₀₀₁₅ indicating a co-existence of α-U and γ-U phase. The single γ-U phase can be obtained in U₀.₇₀Z₀₀₁₃ splat, i.e. at higher Zr content (U-30 at.% Zr). However, a larger broadening of γ-reflections is observed attributed to an additional disorder of Zr atom distribution at such high Zr alloying content.

Figure 1. Temperature dependence of electrical resistivity in zero-field of splat-cooled U-T alloys having the γ-U phase around the superconducting transition temperature. For an easier comparison the curves were normalized to respective resistivity values at 1.5–2 K. The pure single γ-U phase U-15 at. % Mo splat has a highest critical temperature (∆Tc = 2.11 K) and sharpest resistivity drop (∆ρc = 0.02 K).

Our recent investigations indicate that alloying with Ti leads to a similar situation, i.e. a co-existence of α-U and γ-U phase in U₀.₈₅T₀₀₁₅ and a single γ-U phase but with a large peak-broadening for U₀.₇₀T₀₀₃₀. Alloying with 15 at.% Ru leads to a stabilization of the pure γ-U phase revealed by single and sharp γ-U peaks in the XRD pattern of U₀.₈₅Ru₀₀₁₅.

Another clear evidence for the γ-U phase is the negative temperature coefficient of electrical resistivity (dρ/dT < 0) in the normal state. Namely, a weak decrease of the electrical resistivity with increasing temperature was observed, similar to that in strongly disordered alloys and compounds [13, 14]. Despite of some small differences in the absolute values of residual resistivity (ρ₀) and the room-temperature resistivity (ρ₃₀₀K), the relative change of the resistivity with temperature is similar for U₀.₈₅T₀₀₁₅ alloys (T = Mo, Pt, Nb, Ti). The negative slope is attributed to a weak localization, which appears under conditions of strong disorder and which is partly suppressed by electron-phonon scattering. In the case of U₀.₇₀Z₀₀₃₀ containing the γ-U phase, the negative slope does not develop yet. Instead a positive slope was observed. However, the dρ/dT value is almost close to zero. We expect that the negative slope may develop at higher Zr concentrations than 30 at.%.

All investigated U-T splats become superconducting below 2.2 K. The superconducting transitions revealed by abrupt resistivity drops in zero magnetic field are shown in figure 1. In the pure U splat, the transition is manifested by a single drop at Tc = 1.24 K with a transition width ∆Tc = 0.2 K. The highest critical temperature Tc = 2.11 K and the sharpest resistivity drop at Tc (∆ρc = 0.02 K) was found for U₀.₈₅Mo₀₀₁₅. U₀.₈₅Nb₀₀₁₅ becomes superconducting at Tc = 1.90 K (with ∆Tc = 0.15 K), i.e. at similar critical temperature as for U-Mo alloys consisting of γ-U structure with 11–12 at.% Mo alloying. Despite of a similarity in the crystal structure with U₀.₈₅Mo₀₀₁₅, a lower critical temperature and a wider transition (Tc = 1.46 K, ∆Tc = 0.07 K) was found for U₀.₈₅Ru₀₀₁₅.
U_{0.85}T_{0.15} becomes superconducting at $T_c = 0.99$ K. We notice here that $U_{0.85}T_{0.15}$ contains the mixed ($\alpha + \gamma$)-U phase. However, only a single drop was observed at $T_c$. The transition width in this case is quite large ($\Delta T_p = 0.15$ K). The superconductivity in $U_{0.85}P_{0.15}$ is characterized by a sharp drop at $T_c = 0.61$ K (with $\Delta T_p = 0.04$ K). In fact it is the lowest critical temperature for all investigated U-T splats in our case. In addition, a second small drop was observed at $T_c(h) = 0.95$ K (with $\Delta T_p = 0.08$ K). We notice here that a complicated phase situation was detected for the U-15 at. % Pt splat at the grain boundaries [11]. Besides, although the XRD patterns did not reveal any reflection characteristic for UPT phase, we cannot exclude its existence. Thus we cannot be conclusive about intrinsic behavior of UPT. We note here that, even if for the $U_{0.95}P_{0.05}$ (U-5 at. % Pt) splat [15] and $U_{0.85}T_{0.15}$ splat consisted of a mixed $\alpha$-U and $\gamma$-U phase, the superconducting phase transition is revealed by only a single drop in the resistivity. More detailed investigations of superconducting phase transition in UPT alloys are in progress. We add in the same figure the data for $U_{0.72}Zr_{0.30}$ splat consisting of $\gamma$-U phase which exhibits a superconducting transition revealed by a single drop at $T_c = 0.81$ K (with $\Delta T_p = 0.08$ K), for a comparison.

Applying external magnetic fields, the superconducting transitions shift towards lower temperatures, as expected. The estimated values for critical magnetic fields at zero temperature ($\mu_0H_c$) and the critical slopes at $T_c$ of the $H_c2$ versus $T$ curves ($-\mu_0\delta H_c2/\delta T\vert_{T_c}$) are respectively in the range of $2 - 7$ T and $2 - 4$ T(K).

For most of investigated alloys, only a very small feature (i.e. a weak but non-negligible and broad bump) related to the superconducting transition was revealed in the specific heat at $T_c$. The pronounced $\lambda$-type specific-heat anomaly was observed only for U-15 at. % Mo splat. In this case, the height of the experimentally observed specific-heat jump ($\Delta C$) is in a good agreement with that estimated from BCS theory.

4. Nanocrystalline $\beta$-UH$_3$ structure in (UH$_3$)$_{0.85}$Mo$_{0.15}$

We have thoroughly investigated hydrogenation of splat-cooled U-Mo alloys. For the low Mo alloying range, e.g. $U_{0.96}Mo_{0.04}$, for which the alloy consists mostly the orthorhombic $\alpha$-U structure, hydrogenation led to a formation of the $\beta$-UH$_3$.
The temperature dependence of magnetization of (UH₃)₀.₈₅Mo₀.₁₅ indicates the ferromagnetic ordering with the Curie temperature \( T_C \) close to 200 K. The spontaneous magnetization is estimated to be \( M_s = 1.15 \mu_B/U \), certainly higher than that for \( \beta \)-UH₃ (~0.₉ \mu_B/U [6, 18]), but much lower than the ionic moments (~3.₂ \mu_B for \( f^2 \) or \( f^3 \) ground state). Thus it is attributed to the strongly itinerant magnetism of the U hydrides. Our \emph{ab initio} calculations [19] suggested a depopulation of the U-6d and 7s states. It may be the clue to the 5f band narrowing and strong ferromagnetic features in the hydrides.

The surprising fact is the enhancement of \( T_C \) in the hydrides of U-based alloys with \( \gamma \)-U phase. It is in contrary with earlier observation revealing that a reduction of the crystalstallinity implies a suppression of the 5f magnetism in U-based systems [20]. (UH₃)₀.₈₅Mo₀.₁₅ is probably the first U-based ferromagnet with such a high Curie temperature reaching 200K.

An anomaly is clearly revealed around \( T_C \) in the temperature dependence of the specific heat of (UH₃)₀.₈₅Mo₀.₁₅, as shown in figure 5. For a comparison, we show also the literature data of \( \beta \)-UH₃ [6]. It indicated that the ferromagnetic transition in (UH₃)₀.₈₅Mo₀.₁₅ shifted to higher temperature (i.e. at 200 K compared with that of \( \beta \)-UH₃). Besides, a visible peak broadening is observed, attributed to e.g. the grain distribution due to disorder in the sample. The Sommerfeld coefficient of the electronic specific heat can be estimated from the low-temperature part of the specific heat by the Debye model (\( \gamma_e = 29.2 \text{ mJ K}^{-2} \text{ mol}^{-1} \), or \( \gamma_e = 34.4 \text{ mJ K}^{-2} \text{ U}^{-1} \), see table 1). The increase of \( \gamma_e \) in the hydride with respect to initial alloy is a clear evidence of an increase of the density of states at the Fermi level attributed to an enhancement of the U–U spacing and consequent narrowing the 5f band.

5. Crystalline \( \alpha \)-UH₃ structure in (UH₃)₁₋ₓZrₓ

The atomic radius of Zr (1.₆₀ Å) is larger than that of U (1.₅₆ Å), while that of Mo (1.₄₀ Å) is smaller. Thus Zr doping would imply a lattice expansion and an increase of the shortest interuranium distance (see table 1), i.e. an opposite effect to that of Mo doping. Similar to Mo alloying, Zr alloying leads to a rapid suppression of numerous \( \alpha \)-U peaks and development of \( \gamma \)-U peaks seen in XRD pattern. However, unlike U-Mo alloys, the \( \gamma \)-U phase can be stabilized in U₀.₇₀Zr₀.₃₀ splat, i.e. at a much higher Zr content.

U-Zr alloys are very stable at the ambient temperature and ambient pressure. The hydrogen absorption takes place only upon applying high pressure >2.₅ bar and single phase hydrides of the type (UH₃)₁₋ₓZrₓ, are formed [19]. XRD patterns of the (UH₃)₁₋ₓZrₓ hydrides as well as of their precursors are presented in figure 6. As examples, we show the data for \( x = 0.₁₅ \) (admixture (\( \alpha \)+\( \gamma \))-U) and \( x = 0.₃ₐ \) (pure \( \gamma \)-U). Unlike the Mo doped hydrides, the XRD patterns for the Zr doped hydrides reveal the crystalline state, which is
clearly different from $\beta$-UH$_3$. Detailed analysis provides a bcc structure, which is very much expanded (by 75% in volume expansion) with respect to the bcc precursor. The lattice bcc structure, which is very much expanded (by 75% in volume expansion) with respect to the bcc precursor. The lattice parameters $a = 4.16$ Å, very close to the $\alpha$-UH$_3$ structure.

A small amount of ZrC impurity was also observed for all hydrides. We remind here that hydride formed from the pure U splat shows an admixture of ($\alpha + \beta$)-UH$_3$ in which $\beta$-UH$_3$ is a dominant phase. Adding Zr, the concentration of $\alpha$-UH$_3$ phase was found to increase, while that of $\beta$-UH$_3$ decreases. For $x = 0.15$, only tiny peaks of residual $\beta$-UH$_3$ could be observed. For $x = 0.20$, 0.30, no $\beta$-UH$_3$ was observed. The XRD patterns revealed only reflections attributed to $\alpha$-UH$_3$ without $\beta$-UH$_3$ admixture. The peaks, however, are much broader. Detailed analysis indicates a grain size in the range of 10–20 nm, which was in a good agreement with that revealed in the TEM micrograph [16].

We remind here again that $\alpha$-UH$_3$ has never been so far stabilized in a pure form. By hydrogenation of Zr doping alloys with stabilized cubic $\gamma$-U phase, we are able to prepare and investigate the pure $\alpha$-UH$_3$ without any $\beta$-UH$_3$ admixture.

The ageing was observed for the hydrides with low Zr concentration, e.g. after one month, the $\alpha$-UH$_3$ phase in pure-U hydride and in (UH$_3$)$_{0.89}$Zr$_{0.11}$ has been partly transformed to $\beta$-UH$_3$ structure. We remind here again that $\alpha$-UH$_3$ has never been so far stabilized in a pure form. By hydrogenation of Zr doping alloys with stabilized cubic $\gamma$-U phase, we are able to prepare and investigate the pure $\alpha$-UH$_3$ without any $\beta$-UH$_3$ admixture.

In both cases (of Mo as well as Zr doping), the $T_C$ dependence on Mo/Zr concentration revealed a maximum around the concentration range of 12–15 at.%. In the $\beta$-UH$_3$ structure type with 8U atoms in an unit cell, a periodic replacement of one of U atoms by Mo would yield (U$_{0.875}$Mo$_{0.125}$)$_3$H$_3$, which is just at about the Mo concentration at which the maximum in $T_C$ was revealed (e.g. in (UH$_3$)$_{0.88}$Mo$_{0.12}$). However, such a tendency cannot be applied to the Zr system containing $\alpha$-UH$_3$ structure type (with 2 U atoms in a unit cell), since the maximum appeared at a similar metal content. We notice also that the H concentration was found to be scaled rather with U concentration, but not with metal atoms (i.e. (UH$_3$)$_{1-x}$ formula).

All hydrides exhibit very wide hysteresis loops. As example, the hysteresis loop of (UH$_3$)$_{0.85}$Zr$_{0.15}$ measured at 2 K was shown in figure 8 which has a rectangular shape with a width of about 8 T. Increasing Zr concentration from 0 to 30 at.% implies an increase of the width of the loop. It reaches 11 T for (UH$_3$)$_{0.70}$Zr$_{0.30}$. Below 6 K, the loops for hydrides of both Zr as well for Mo system revealed erratic steps. For instance, many small Barkhausen-type reproducible jumps (due to domain wall pinning) in the loop have been revealed for (UH$_3$)$_{0.85}$Zr$_{0.15}$ in the field range 3–4 T at 2 K. For a comparison we show in the same figure the loop of (UH$_3$)$_{0.85}$Mo$_{0.15}$

Figure 6. (a) XRD pattern of U$_{1-x}$Zr$_x$ alloys ($x = 0.15, 0.30$, i.e. U-15 at.% Zr and U-30 at.% Zr). A pure $\gamma$-U phase is obtained only for $x = 0.30$. (b) XRD pattern of (UH$_3$)$_{1-x}$Zr$_x$ revealed reflections attributed to $\alpha$-UH$_3$. For a comparison, the $\alpha$-UH$_3$ and $\beta$-UH$_3$ diffraction lines are included.

Figure 7. Temperature dependence of magnetization of (UH$_3$)$_{0.85}$T$_{0.15}$ ($T = $ Zr, Mo) measured in magnetic field of 0.05 T (in the field-cooled mode) and 4 T.

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Figure 7. Temperature dependence of magnetization of (UH$_3$)$_{0.85}$T$_{0.15}$ ($T = $ Zr, Mo) measured in magnetic field of 0.05 T (in the field-cooled mode) and 4 T.

In both cases (of Mo as well as Zr doping), the $T_C$ dependence on Mo/Zr concentration revealed a maximum around the concentration range of 12–15 at.%. In the $\beta$-UH$_3$ structure type with 8U atoms in an unit cell, a periodic replacement of one of U atoms by Mo would yield (U$_{0.875}$Mo$_{0.125}$)$_3$H$_3$, which is just at about the Mo concentration at which the maximum in $T_C$ was revealed (e.g. in (UH$_3$)$_{0.88}$Mo$_{0.12}$). However, such a tendency cannot be applied to the Zr system containing $\alpha$-UH$_3$ structure type (with 2 U atoms in a unit cell), since the maximum appeared at a similar metal content. We notice also that the H concentration was found to be scaled rather with U concentration, but not with metal atoms (i.e. (UH$_3$)$_{1-x}$ formula).

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revealed, as shown as an example the loop at 54 K. At higher temperatures a smooth behavior was observed up to 6 K. At higher temperatures a smooth behavior was measured at around 2 K. The curves with erratic steps were 30–40% of that expected from BCS theory (marked by the anomaly was observed at around 1.7 K), which exhibit a different tendency. Namely, only a single abrupt Barkhausen-type reproducible jump appears between 3.6 and 3.7 T followed by a more smooth increase at higher fields. Besides, all the loops reveal a very slow approach to saturation.

The difference in demagnetization behavior at low temperatures could be in the crystal structure. Namely, in (UH₃)₀.₇₀Zr₀.₃₀ there is a crystalline structure, the magnetic moments are more collinearly arranged and thus have a higher crystalline anisotropy. As a result, domains have narrow walls and can be easily pinned at the grain boundaries. The remagnetization can happen in many grains at the same time implying erratic steps of magnetization. The situation is different in (UH₃)₀.₇₀Mo₀.₃₀ with the nanocrystalline structure and thus with a random orientation of local easy-magnetization directions and with a very small anisotropy. The magnetization processes can be very complicated in this case, i.e. for nanostructured inhomogeneous ferromagnet. It takes smaller magnetic fields to demagnetize the whole sample.

In both cases, the coercive field reaches very high values at low temperatures, μ₀Hₑₑ ≈ 4–6 T were found below 3 K. The high magnetic anisotropy is related to large orbital moments in bonding 5f states. At higher temperatures than 6 K, smooth hysteresis loops were observed in all cases. As example, we show also in figure 8 the smooth hysteresis loop observed at 54 K for (UH₃)₀.₇₀Mo₀.₃₀. The main point is that the loop does not reach the reversible behavior even at 12 T.

The specific heat measurements in the temperature range of 0.4–300 K were performed on both hydride samples of Zr doped alloys as well their precursors (UZr alloys). A visible anomaly was observed at around Tₑₑ values determined from the electrical resistivity jumps, revealing that the superconductivity in this splat is a real bulk effect. However, unlike the case of U-Mo alloys, no λ-type peaks was observed in splat-cooled UZr alloys, only very broad bumps were revealed. Indeed, the most visible bump observed for of U₀.₇₀Zr₀.₃₀ alloy is shown in figure 9. The value of the jump amounts to only 30–40% of that expected from BCS theory (marked by the vertical bar in the figure). Only a broader and smaller feature related to Tₑₑ was observed in the hydride (UH₃)₀.₇₀Zr₀.₃₀. Similar to hydride of Mo doped alloys, an enhancement of the Sommerfeld coefficient of the electronic specific heat was obtained in the hydride of Zr doped alloys (with respect to initial alloy) indicating an increase of the density of states at the Fermi level due to an increase of the U–U spacing.

We notice here that no sign of hydride was observed in XRD patterns after the desorption at 800 °C (1073 K) with a subsequent evacuation of reactor. In other words, the hydride is transformed back to the γ-U phase with a presence of UC and UO₂ impurities. In the case of a desorption at 500 °C (773 K), apart from γ-U, UC and UO₂, a large portion of the α-U phase was obtained as a consequence of α–γ phase transformation at this temperature.

6. Concluding remarks

Our study indicates that the UH₃-based materials can exhibit a large flexibility of the crystal structure and chemical composition. However, beside of some difference in the character of hysteresis loop between Mo and Zr alloyed hydrides (which depends on e.g. grain size) e.g. the unexpected enhancement the ordering temperatures Tₑₑ, the variations of magnetic properties (such as the U moment and Tₑₑ) are quite similar. The stoichiometry always corresponds with approx. 3H atoms per 1 U atom. We suggest that uranium and hydrogen form well defined structure units, which are only weakly affected by alloying atoms and that the U–H interaction may play a dominant role instead of U–U separation and related band effects.

Hydrogenation of Mo doped alloys with cubic γ-U phase implies a formation of a new structure form of β-UH₃, the nanocrystalline structure. The pure crystalline α-UH₃ structure with any admixture β-UH₃ has been formed and thus can be studied for the first time by hydrogenation of Zr doped alloys with γ-U phase. Despite of different crystal structure
and inter-U spacing, the electronic and magnetic properties of α-UH₃ are very similar to those of β-UH₃.

It is still not clear if such hydrides formed from γ-U alloys can be considered as novel materials for hydrogen storage applications. However, in the context of practical application, our study indicates an easy route for producing the γ-U alloys in a powder form: by a combination of hydrogenation, followed by crushing of the brittle hydrides into powders and then by hydrogen desorption (of the powders) in a vacuum.

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