1. Introduction

Uranium is present in most nuclear fuels and thus its crystal structure and physical properties have been thoroughly investigated. However, the low-temperature properties of uranium have been mostly known for the orthorhombic \( \alpha \)-U phase (space group \( \text{Cmcm} \)), since only this phase is stable at and below room temperature [1], e.g., it exhibits a superconducting state below the critical temperature \( T_c = 0.78 \text{K} \) [2, 3]. Besides the orthorhombic \( \alpha \)-U phase, there are two other allotropic phases of uranium: the \( \beta \)-U phase with a tetragonal structure (space group \( \text{P}4_2 = \text{mmm} \)) and the \( \gamma \)-U phase with a body-centered-cubic structure (space group \( \text{Fm}3m \)) which are stable at temperatures in the range of 940–1045 K and 1045–1405 K, respectively.

Numerous studies have been carried out on alloys consisting of \( \beta \)-U and \( \gamma \)-U phase since the 1960s, but mostly from the viewpoint of metallurgy. The \( \gamma \)-U phase alloys in particular have been considered as promising candidates for low-enriched uranium nuclear fuels used in research nuclear reactors [4, 5]. It is known that the \( \gamma \)-U phase can be stabilized...
down to room temperature by alloying with 4d and 5d elements from group 4 to 8 of the periodic table, such as Zr, Mo, Nb, Pd and Pt [6]. However, their physical properties, especially at low temperatures, have not been investigated and thus are not known.

Recently, we have succeeded in the stabilization of γ-U phase by alloying with various elements in combination with the splat-cooling technique [7, 8]. Thus, we could investigate the low-temperature thermodynamic properties of such systems [9, 10]. Our second goal is to investigate the possibility of hydrogen storage of the γ-U phase and its stability. It is well known that the (pure) natural uranium (consisted of the orthorhombic α-U phase) easily absorbs a large amount of hydrogen forming uranium-trihydride (UH$_3$). However, such formed UH$_3$ is a nasty pyrophoric powder which self-ignites in air [1]. Our recent investigations have shown that the U–T alloys containing the γ-U phase (so-called the γ-U alloys) are stable in air and hydrogen exposure at atmospheric conditions. They can absorb a large amount of hydrogen but only upon applying hydrogen pressure higher than 2.5 bars. The formed hydrides (UH$_3$)$_x$–T, are ferromagnets with the Curie temperature reaching 200 K [11, 12]. The crucial point is that the hydrides formed from the γ-U alloys are very stable in ambient conditions and in particular they are non-pyrophoric. Thus it is very safe and easy to handle them. Besides, it is very easy to release the hydrogen by desorption of the hydrides in vacuum. The hydrogen amount is always about 3 H atoms per 1 U atom.

We extend our investigations on the U-based alloys with the γ-U phase by Pt alloying, especially their hydrogen storage capacity. Large attention has been focused on the rich-Pt part of the uranium-platinum (U-Pt) system, in particular on the 4 intermetallic compounds, UPt, UPt$_2$, UPt$_3$ and UPt$_5$ [13]. The low-Pt part (with Pt concentration $< 50$ at.% (atomic percent)) of the U-Pt system has been much less studied. To the best of our knowledge, except for old reports focused mostly on the phase diagram and crystal structure with the information that Pt has only about 2–5 at.% solubility in the γ-U phase at the eutectic temperature, there is no report of the basic thermodynamic properties of the U-Pt system with low Pt concentrations, in particular those consisting of γ-U phase. For a recent review of the U-Pt system, see the introduction of reference [14].

We recall here that many materials exhibit superconducting phase transitions and other spectacular features in the temperature range of millikelvin (mK). From a fundamental research viewpoint, it is very important to gain information about the ground state of such materials. Experiments at the mK temperature range are now available in Krakow by means of the Closed Cycle Dilution Refrigerator Triton from Oxford Instruments, in the Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology. Pre-cooling of the mixing chamber and the superconducting magnet is ensured by the pulse-tube cooler operating in a closed cycle. The base temperature would be limited by the cooling power of the dilution refrigerator, which is typically 1 mW at 30 mK.

In the present work we present our investigations of the electrical transport in mK ranges in applied magnetic fields of U-Pt alloys with Pt concentration ≤ 15 at.% prepared by the ultra-fast cooling technique. Prior to hydrogenation experiments on this system and study of the hydrogen absorption, we first investigate the structure and the electronic properties of the splat-cooled U-Pt alloys, i.e., the metallic precursors of the hydrides, especially those consisting of the γ-U phase. The use of Triton is highly desirable, since the U-Pt splats revealed the lowest critical temperatures among all U-based splats, especially as it shifts down below 400 mK—the temperature limit of Quantum Design physical properties measurement system (PPMS) commonly used for low-temperature measurements.

2. Experimental

The sample-ingots with a typical sample mass of 200–300 mg of U-Pt alloys with Pt concentration up to 15 at.% were prepared by arc melting of high-purified elements (e.g. U with 2N8 purity and Pt with 3N5 purity). Splat-cooled samples (splits) were produced from such sample-ingots by means of a high-vacuum (HV) splat cooler (Vakuum Praha). This technique allows one to achieve a cooling rate better than 10$^6$ K s$^{-1}$, which is fast enough in 'freezing' the high-temperature phase and thus stabilizing it down to room temperature. More details of the splat-cooling technique and sample preparations were described in our previous papers (e.g. [7]). Throughout our work, we use the atomic percent (at.%) to indicate the concentrations, e.g. U-15 at.% Pt stands for U$_{0.85}$Pt$_{0.15}$.

Unlike other U–T alloys (T = Mo, Zr, Nb), the preparation of splats of the U-Pt alloys is very tricky. At standard setting parameters of the HV splat cooler, we can easily obtain the proper splat-cooled discs with a thickness of 100–150 µm for the Pt concentrations up to 5 at.%, while the splat formation turned out to be very difficult for higher Pt concentrations. In most cases, splats with much higher thickness (> 250 µm) having elongated shapes inherited from the falling drops were obtained (due to a much slower cooling rate than the expected rate of 10$^6$ K s$^{-1}$). The proper splats (i.e. the 100–150 µm-thick discs) revealing a proper cooling rate (of 10$^6$ K s$^{-1}$) could be obtained only after many attempts by varying the setting parameters of the splat cooler as well as the sample mass.

The crystal structure of samples was examined by x-ray diffraction (XRD) using the Bruker D8 Advance diffractometer with Cu-K$_\alpha$ radiation. Additional phase purity analysis was performed by means of x-ray energy dispersive microanalysis (EDX) using the scanning electron microscope (SEM) FEI Quanta 200 FEG (field emission gun). The splats show in most cases a homogeneous distribution of the alloying elements with concentrations corresponding to the nominal ones.

For the temperature range from 0.4 K up to 300 K, we use the Quantum Design PPMS in applied magnetic fields up to 7 T for the electrical resistivity and the specific-heat measurements. The electrical resistivity measurements using the $ac$ technique in a standard four-probe configuration in the range of 30 mK–300 K were carried out in a Triton $^3$He/$^4$He dry dilution refrigerator. Pre-cooling of the mixing chamber and the superconducting magnet is ensured by the pulse-tube cooler operating in a closed cycle. The base temperature...
(8 mK with installed measurement stage at mixing chamber plate) is achieved by condensing the $^3$He/$^4$He and then through continuous evaporation and compression of the pure $^3$He phase. The superconducting magnet mounted in Triton during measurements stays at the temperature 3.1 K, and can be used to obtain magnetic fields up to 14 T. An Ametek SR7270 lock-in nanovoltmeter served both as a source of a current and as a voltmeter of the signal. All dependences were measured for a current of 100 $\mu$A at a frequency of 123 Hz. The electrical contacts between sample and sample holder were made by a wedge bounding technique with 25 $\mu$m thick aluminium wire by TPT HB05 bounder. The resistance of those contacts were lower than 0.1 $\Omega$.

To underline the influence of the cooling rate on the structure and electrical drops at the superconducting phase transition, we performed experiments on the two splats having the same Pt concentration of 15 at.% revealing the cubic $\gamma$-U phase: the proper splat (a disc-shape splat), the drop-like splat (the splat with elongate-shape with thicker thickness due to a much lower cooling rate).

3. Results and discussion

Similar to other splat-cooled U–T alloys, the XRD patterns of U-Pt splats in an as-formed state revealed a gradual decrease of the intensity of orthorhombic $\alpha$-U reflections and a development of $\gamma$-U reflections with increasing Pt concentration. Detailed analysis of the structure changes as a function of Pt concentration in the range of 0–15 at.% in U-Pt splats has been reported [10, 15]. In brief, using splat cooling technique, we can extend the solubility of Pt in $\gamma$-U at least up to 15 at.%, i.e. much higher concentrations of alloying Pt than that reported earlier (5 at.%). Moreover, we can also retain the cubic $\gamma$-U phase in U-15 at.% Pt alloys down to room temperature and thus can investigate the low-temperature properties.

The crystal structure investigations by XRD of different U-15 at.% Pt alloys revealed that: (1) the proper splats (the thin splats with a thickness below 150 $\mu$m) contain the cubic $\gamma$-U phase with a trace of $\alpha$-U phase, (2) the thick splats (with a thickness >400 $\mu$m) show a similar structure to that of the bulk-sample (the precursor of the splat) consisted of a mixture of the $\alpha$-, $\beta$- and $\gamma$-U phases and (3) the drop-like splats (with a thickness in the intermediate range of 200–400 $\mu$m) reveal an intermediate behaviour between these two above limits, e.g. with an enhancement of the $\alpha$-U reflections and with a more broadening of $\gamma$-U reflections (in comparison with that of the proper splats). We explain it as a consequence of slower cooling in the thicker splats and consequently a smaller fraction of the $\gamma$-U phase in the drop-like splats [14].

Microstructure analysis was performed on the proper splat of U-15 at.% Pt containing the dominant $\gamma$-U phase [14]. The back-scattered diffraction (BSD) images are shown in figure 1. X-ray energy dispersive (EDX) microanalysis reveals that the material consists mostly of a single phase with bimodal microstructure with grain sizes of 1–5 $\mu$m (figure 1(a)). The BSD analysis indicates that the main part of the splat—the interior
of the grains (in grey-color) corresponds to the nominal 15 at.% Pt concentration. The black-colored part is uranium oxides, nitrides or carbides. The most complicated situation is at the grain boundaries (figure 1(b)). Analyzing its volume, we arrive at an average Pt concentration of 26 at.%, indicating that the grain boundaries tend to be enriched with Pt. The almost white isolated nanoparticles (nanocrystals) of the size of 100 nm are the Pt-rich ones, which are embedded in a darker area (than the grain-interior grey phase), which are certainly U-rich, attributed to the α-U like-phase. One can also see the fine lamellas propagating from the grain boundaries into the grain interiors which represent Pt-concentration fluctuations on a length scale of 20–50 nm. The volume fraction of the grain boundaries is only a few percent. Thus its contribution can be hardly revealed in the XRD patterns. However, it could have a large influence on the transport properties.

Similar to U-Mo splats, the temperature dependence of electrical resistivity of the splat-cooled U-Pt alloys reflects the atomic disorder, which leads to a dramatic enhancement of residual resistivity and a change of the ρ(T) dependence from the typical metallic behaviour (for low Pt concentrations ≤10 at.%) with a positive temperature coefficient (dρ/dT > 0) to the negative temperature coefficient (dρ/dT < 0) for U-15 at.% Pt (proper splat) [14, 15]. We recall here that our investigations indicate that dρ/dT < 0 appears only in U-T alloys with the cubic γ-U structure.

All investigated U-Pt samples become superconducting below 1.1 K. The superconducting transitions revealed by resistivity drops in zero magnetic field are shown in figure 2. For a comparison, we show the normalized curves with respect to the resistivity values in the normal state, the ρ(T)/ρ_{1.2 K} curves. For U-5 at.% Pt and U-10 at.% Pt, the superconducting transition was revealed by a single drop respectively at 0.70 K and 1.03 K with a very small transition width ΔT_{ρ} = 0.02 K. For the U-15 at.% Pt proper splat, the superconducting phase transition is manifested by an abrupt drop for which the resistivity value decreases from 90% to zero at T_{c} = 0.61 K with a small transition width ΔT_{ρ} = 0.04 K attributed to the bulk superconducting phase. Besides this transition, an additional feature is observed at a higher temperature T_{c(h)} = 0.95 K with ΔT_{ρ} = 0.08 K (for which the resistivity decreases from 100% (the normal state) to 90%). At first glance, one may attribute the two drops in U-15 at.% Pt splat respectively to the superconducting transitions of the γ-U and α-U phase (since a small portion of the α-U phase does still exist in this splat). Even if some small portion of the intermetallic UPt compound may be present in the sample, it is known to be a ferromagnet, not a superconductor and thus has shown no
contribution to the resistivity features around $T_c$. However, in the splats consisting of a mixture of the ($\alpha + \gamma$)-U phase, such as U-5 at.% Pt and U-10 at.% Pt splat, only a single and sharp resistivity drop was observed. We notice here that in the resistivity, the relative size of the superconducting transition has very little relation to the relative abundance of each phase in the sample. There is a key role of spatial distribution, as e.g. a small amount of superconducting phase situated at the grain boundaries can make an effective short circuit of the whole sample. This seems to be the situation for the U-15 at.% Pt splat. An alternative explanation, assuming two transitions belonging to the same and single phase are interpreted in the context of electronic disorder, as recently observed in e.g. skutterudite-related La$_3$Ru$_4$Sn$_{13}$ [16].

The resistivity versus temperature measured in the applied external magnetic fields are shown in figures 3 and 4. In general, the superconducting phase transitions shift towards lower temperatures with increasing magnetic fields and the characteristics of the $\rho(T)$ curves do not change much. As we have already mentioned, for the U-Pt system, we could get a good splat (with a thickness below 150 $\mu$m, as a result of obtaining the proper cooling rate of $10^6$ K s$^{-1}$ during sample preparations) as well as the drop-like splat (with a thickness of 250 $\mu$m, i.e. in the intermediate thickness range between proper splats and bulk samples, as a consequence of a much slower cooling rate than the expected rate of $10^6$ K s$^{-1}$). In order to get more information about the correlation between the sample technology and its physical properties, we have performed resistivity measurements for two U-15 at.% Pt splats: the proper splat and the drop-like splat, shown in figure 4. We define $T_c$ and $T_c(h)$ respectively as the temperature at the half-height of the resistivity drops. The $\rho(T)$ curves of the drop-like splat clearly reveal a complicated phase situation. Namely, three distinguished resistivity drops are present, which remind us of the occurrence of all three U phases in the bulk material. We also notice here that we observed only one drop bringing the resistivity to zero value in the as-cast bulk sample, the precursor of the splat [14]. However, it does not mean naturally only one phase is present in the sample, rather the phase with the highest $T_c$ is abundant enough to provide a zero resistance current path.

We notice here that the resistivity value in the normal state increases with increasing Pt concentration. For instance, the value at 1.2 K is 44.6 $\Omega$ cm, 69.8 $\Omega$ cm, 104.1 $\Omega$ cm and 164.2 $\Omega$ cm respectively for 2, 5, 10 and 15 at.% Pt concentration, indicating an increasing atomic disorder. Besides, the ultra-fast cooling could affect the grain size and thus could produce some additional disorder.

The temperature dependence of the upper critical fields $H_{c2}$ in the $H$–$T$ phase diagram for the UPt splats is shown in figure 5. The characteristic of the $H$–$T$ diagram is quite similar, except for the difference in the critical field values. For U-15 at.% Pt splats, we show the values estimated both for the high-temperature and low-temperature superconducting transitions in the proper splat as well as in the drop-like splat. The crucial point is that by means of the Triton apparatus with the possibility of performing measurements down to 50 mK, we would be able to collect more data points for the UPt splats revealing low values of $T_c$, especially in applied magnetic fields and thus it is possible to make the best fits of the data points. In all cases, reasonable fits to the Ginzburg-Landau theory approximation [14] are obtained. It provides the estimated values for the critical magnetic field at 0 K ($\mu_0H_{c2}(0)$) and the critical slopes at $T_c$ of the $H_{c2}$ versus $T$ curves ($-\mu_0dH_{c2}/dT_{c}$) in the range of 1–5 T and 2–4 T K$^{-1}$, respectively, similar to those found for other splats of U-based alloys.

The temperature dependence of specific heat, $C_p(T)$, has been performed on U-5 at.% Pt and U-15 at.% Pt (proper) splat for the temperature range 0.4–15 K. The Sommerfeld coefficient of electronic specific heat and the Debye temperature are estimated to be $\gamma = 19.5$ mJ K$^{-2}$ mol$^{-1}$ ($\approx 22.9$ mJ K$^{-2}$ mol$^{-1}$ U), $\Theta_D = 145$ K for U-15 at.% Pt [10]. It indicates a large softening of the lattice (revealed by reduction of Debye temperature) and a large enhancement of density of states at the Fermi level $D(E_F)$ by Pt alloying.
dependence of specific heat around the superconducting phase transition is shown in figure 6. For both splats, the superconducting transition is revealed by only a weak and broad bump in the \( C(T) \) curve. Using the \( \gamma_c \) and \( T_c \) values from our experiments, we estimated the specific-heat jump expected from the BCS theory, shown by vertical bars in figure 6. In both cases, the specific-heat jumps are much smaller than the calculated values. For instance, for U-5 at.% Pt, the experimental jump amounts only to 22% of the BCS value.

For U-15 at.% Pt proper splat (splat) and for drop-like splat (drop), we show the values estimated both for the high-temperature (high \( T \)) and low-temperature (low \( T \)) superconducting transition. The fits by second-order polynomial function are shown by solid lines.

4. Conclusions

All investigated splat-cooled U-Pt alloys with Pt concentration \( \leq 15 \) at.% become superconducting below 1.1 K revealed by abrupt resistivity drops with small transition widths of 0.02–0.04 K. U-15 at.% Pt proper splat exhibits the lowest superconducting temperature at \( T_c = 0.61 \) K. The estimated values for the critical magnetic field at 0 K (\( \mu_0H_c (0) \)) and the critical slopes at \( T_c \) of the \( H_c2 \) versus \( T \) curves (\( \mu_0(\partial H_c2/\partial T)_{T_c} \)) are respectively in the range of 1–5 T and 2–4 T K\(^{-1}\). The \( H-T \) diagram of UPt splats fit well to the Ginzburg-Landau theory approximation. However, the specific-heat jumps are much smaller than the calculated values from the BCS theory.

The crucial point is that by using ultrafast cooling we could extend a higher solubility of Pt metal in \( \gamma \)-U, up to at least 15 at.% Pt, and stabilize this cubic \( \gamma \)-U phase at room temperature. We could then perform investigations of its properties and thus add new data to the database.

We emphasize again that all of the investigated splat-cooled U-Pt alloys were obtained without any additional treatment and that they are very stable when exposed to ambient conditions: no ageing or phase transformation/decomposition was observed. Besides, all splats have a high resistance and that they are very stable when exposed to ambient conditions. We could then perform investigations of its properties and thus add new data to the database.

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