Superconductivity in the splat-cooled UMo alloys

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Abstract
We have investigated the superconductivity in splat-cooled UMo alloys by low-temperature resistivity and specific-heat measurements down to 0.4 K. The γ-U materials, such as U-Mo15 (with 15 at.% Mo doping), exhibit a conventional BCS superconductivity with $T_c = 2.1$ K and upper critical field exceeding 5 T, much higher than that for α-U materials. The alloys with <10 at.% Mo doping consist of a mixed γ + α-U phase. The superconducting transition in the U-Mo6 revealed by a smooth decrease below 1.5 K and a sharp drop at 0.6 K in the resistivity indicating that γ-U grains are embedded in the α-U matrix. The superconductivity transition was revealed by λ-type peak at $T_c$ in the $C(T)$ curve only for U-Mo15, while only one broad peak at $T_c$ in the $C(T)$ curves were observed for other UMo splats. With applying the magnetic fields, the resistivity jumps and specific-heat peaks move to lower temperatures.

Keywords: U-Mo alloys, mixed γ + α-U phase, splat cooling, superconductivity

Mathematics Subject Classification: 1.00, 5.17

1. Introduction

Below the melting point, metallic uranium exhibits three allotropic phases. Below 940 K (and thus it is the room-temperature phase) the α-phase (α-U) with an orthorhombic structure exists, with the space group Cmcm, unit cell parameters $a = 2.854$ Å, $b = 5.870$ Å, $c = 4.937$ Å, the mass density $\rho = 19.07$ g cm$^{-3}$ and the smallest atomic distance $d_{\alpha-U} = 2.837$ Å [1, 2]. Between 940–1045 K, the β-phase (β-U) with a tetragonal structure exists (P4/mmm, $a = b = 10.52$ Å, $c = 5.57$ Å (when extrapolated to room temperature)), $\rho = 18.17$ g cm$^{-3}$, $d_{\beta-U} = 2.889$ Å, while the γ-phase (γ-U) with a body-centered-cubic (bcc) A2-type structure is stable only between 1045–1405 K (Im $\bar{3}m$, $a = 3.542$ Å (when extrapolated to room temperature)), $\rho = 17.94$ g cm$^{-3}$, $d_{\gamma-U} = 3.067$ Å.

The bcc structure of γ-U phase can be stabilized down to room temperature by alloying with 4d and 5d elements in groups IV to VIII of the periodic table, such as Zr, Mo, Nb, Pd, Pt, etc [3]. Zr and Nb will form a complete solid solution with γ-uranium. However, in order to retain the 100% γ-phase at room temperature, a large concentration of these elements is required to be added in the alloy. Pd and Pt, on the other extreme, have only a very small solubility in U (~2 at.%); these two elements will give very stable intermetallic compounds with uranium. Mo has a large solubility in U (~35 at. %) and thus is considered as a good candidate to stabilize γ-U [4].

Uranium metal has been studied thoroughly. However, it concerns only the orthorhombic α-U phase, since only this phase is stable at and below room temperature. Thus, many low-temperature properties are known for this α-U phase, e.g. the superconductivity of (natural) uranium at 1.3 K was first discovered in 1942 [5]. Recent data have reported $T_c = 0.78$ K for uranium [6, 7]. However, no superconductivity was observed in the good-quality single crystals of uranium [8]. A large amount of work has been performed on β-U and γ-U phase alloys since the 1960s, but mostly from the viewpoint of metallurgy, in particular the γ-U phase alloys were considered as promising candidates for nuclear fuels used in the research for nuclear reactors [9, 10]. However, their fundamental thermodynamic properties, especially at low-temperatures, have been largely ignored. There exist only very

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old reports from the 1960s on the superconductivity of bcc \(γ\)-U with Mo or Nb doping around 2 K [11, 12].

We are interested to characterize the low-temperature properties of the cubic \(γ\)-U phase. We focus our attention on the use of alloying and ultrafast cooling (splat-cooling technique) to stabilize the high-temperature \(γ\)-U phase down to room temperature. We have started with Mo doping, due to the fact that Mo has a large range of alloying with uranium. In this work we summarize our investigations of the low-temperature properties of splat-cooled U-Mo alloys, in particular the superconducting phase transition in these splats.

2. Sample synthesis and experimental details

UMo alloys with Mo content in the range of 0–17 at.% were prepared using natural U (2N8 purity or better) and Mo element (3N5) by arc-melting on a copper plate in an Ar atmosphere. The alloys from arc melting furnace were subsequently transferred to the splat cooling system (HV splat cooler by Vakuum Praha) with a cooling rate up to \(10^6\) K s\(^{-1}\).

More details of splat sample preparation have been reported earlier [13–15]. The resulting splat samples had a shape of irregular disc approx. 20 mm in diameter and 0.1–0.2 mm thickness. As an example, a photograph of the splat-cooled sample disc is shown in figure 1. Throughout our work, we use the notation: U-MoX, where X is the Mo content given in the atomic percentage (at.%) [14]. For example, the alloy with 6 at.% molybdenum (approximation 3 wt.% Mo) is denoted as U-Mo6 (i.e. U\(_{0.94}\)Mo\(_{0.06}\)).

The crystal structure of the splat-cooled alloys (splats) was investigated by XRD measurements using the Bruker D8 Advance diffractometer with Cu-K\(α\) radiation. The x-ray diffraction was taken directly from the surface of splats to minimize any possible martensitic transformation in samples by e.g. any mechanical modifications.

The splats were cut by spark erosion into pieces suitable for subsequent physical properties measurements, i.e. rectangular-shaped pieces of approximate 1 \times 3–4 mm\(^2\) and 2 \times 2 mm\(^2\) were used for the electrical resistivity and specific-heat measurements, respectively. The resistivity measurements were carried out in a standard four-probe configuration using a CCR system (in the temperature range 3–300 K without magnetic field) and by means of quantum design physical properties measurement system (PPMS) for low-temperature measurements in applied magnetic fields (0.3–4.2 K, magnetic fields 0–7 T). The specific-heat measurements were also performed by means of PPMS.

3. Results and discussions

We have investigated the crystal structure of UMo splats thoroughly with Mo doping content \(x = 0, 1, 2, 4, 6, 10, 11, 12, 13, 15, 17\) % in order to determine the limit of Mo range for obtaining the pure cubic bcc-U phase. The obtained results have been published elsewhere [13–16]. The main outcome of the crystal structure studies is listed below:

1. The splat-cooled pure-uranium revealed the predominant \(α\)-U structure with rare, isolated \(γ\)-U grains.
2. The cubic \(γ\)-U phase was obtained in splat samples with Mo content \(\geq 13\) at.% Mo in the as-formed state without any additional sample treatment.
3. The mixed-phase \((α′ + γ)\) structure was obtained in the U-Mo splats with Mo content \(\leq 6\) at.% (no shift of the \(α\) reflections), while the alloys with 6–10 at.% Mo revealed the mixed-phase \((α′ + γ)\) structure (with a significant shift of \(α\) reflections ascribed to a large contraction in the \(b\)-parameter of the regular orthorhombic structure).
4. All splat-cooled materials are very stable in exposure in air. Namely, no aging effect or phase transformation/decomposition was observed.
5. Unlike the \(α\)-U which easily absorbs hydrogen even at room temperature forming \(UH_3\), the cubic \(γ\)-U phase is very stable in exposure in hydrogen atmosphere at pressures below 1 bar and at room temperature, even if after many days.
6. Under higher \(H_2\) pressure (\(>4.5\) bar), hydrogen was absorbed into U-Mo15 (or UMo\(_{0.18}\)) forming hydride \(UH_3\) revealing amorphization. We notice here that, unlike the fine powder of \(UH_3\), the fine powder from \(UH_3\)Mo\(_{0.18}\) is not pyrophoric and its handling is very safe.

In order to investigate the superconducting transitions, we have performed the resistivity and specific-heat measurements down to 400 mK. All UMo splats become superconducting. The critical temperature determined from electrical resistivity measurements in zero field decreases with decreasing Mo concentration \(T_c = 2.11\) K, 1.91 K, and 1.24 K for 15 at.% Mo, 12%, and 0% (pure-U specimen) [13, 16], as shown in figure 2. All curves are normalized to the resistivity value at 4 K. The resistivity values of investigated UMo splats at room temperature and at 4 K are given in table 1. The maximum value correlates well with those of Chandrasekhar and Hulm [11], who reported that \(T_c\) decreases again with more Mo doping. The superconducting phase transition seen in resistivity is quite abrupt, especially for the 15% Mo sample. In order to evaluate the sharpness of the resistivity

![Figure 1](image-url)
jump, we define the width of the superconducting transition as $\Delta T_p = T(\rho_{90\%}) - T(\rho_{10\%})$, where $T(\rho_{90\%})$ and $T(\rho_{10\%})$ is the temperature value at which the respective resistivity amounts to 90% and 10% of that at 4 K. For U-Mo15 $\Delta T_p$ was estimated to be only 0.02 K [13, 15] indicating a particular sharp superconducting transition for the $\gamma$-U phase. The mixed phase U-Mo6 splat reveals clearly two different jumps in the resistivity. The resistivity decreases smoothly from 90% to 50% with decreasing temperature from 1.4 K down to 0.79 K. Then a sharp drop from 50% to 10% was observed at a temperature of 0.77 K. We assume that the first superconducting transition is very smooth with $T_c = 0.90$ K (taken as the mid-point of the first decrease of the resistivity (from 90% to 50%)) and with a larger transition width of $\Delta T_p = 0.60$ K, while the second superconducting transition is very abrupt at $T_c = 0.78$ K (taken as the mid-point of the second decrease of the resistivity (from 50% to 10%)) and with $\Delta T_p = 0.02$ K. The obtained results indicate that there are two distinguishable superconducting phases in U-Mo6 splat. Or in other words, each of the phases in the mixed $\alpha + \gamma$ phase in this alloy exhibits its own superconductivity (possibly with different mechanisms). It forms possibly 3D-network superconductivity similar to that in pure-U (grains consisting of $\alpha$-phase in the bulk and $\gamma$-phase at the boundaries) together with bulk-superconductivity similar to that of U-Mo15 (grains consisted of only single pure $\gamma$-phase). In other words, the $\alpha$-phase grains are embedded in the $\gamma$-phase net.

Applying external magnetic field, the superconducting transitions shift towards lower temperatures as expected. As examples, we show the data obtained for pure-U ($\alpha$-phase), U-Mo6 (the mixed $\alpha + \gamma$ phase) and U-Mo15 (pure $\gamma$-phase) in figure 3. For pure-U splat, the superconductivity is suppressed relatively fast. On the other hand, the $\gamma$-type splats exhibit a much higher field resistance.

Temperature dependence of the specific heat $C_p(T)$ measured for the whole temperature range of 4–300 K. As we reported earlier [15], no significant anomaly related to the charge–density–wave (CDW) transitions in the temperature range of 20–50 K was revealed, either for the splat-cooled uranium specimen or for its bulk precursor. The Sommerfeld coefficient of electronic specific heat $\gamma$ and the Debye temperature $\theta_D$ have been reported elsewhere [16]. We found a significant increase of Sommerfeld coefficient for U-Mo15 splat ($\gamma_c = 16.0$ mJ mol$^{-1}$ K$^{-2}$, i.e. 18.8 mJ mol$^{-1}$ U$^{-1}$ K$^{-2}$), which is clear evidence of an increase of density of states at the Fermi level for $\gamma$-U ascribed to an increased atomic volume and shortened interatomic U–U spacing (affected by the Mo atom dilution into the U lattice) and consequently a narrower 5f-band. The Debye temperature $\theta_D = 139$ K is reduced for $\gamma$-U samples, indicating a softening of the lattice with respect to that for $\alpha$-U ones ($\theta_D = 179$ K).

The low-temperature specific heat ($C(T)$) measurements down to 400 mK are shown in figure 4. The $\lambda$-type specific-heat anomaly marking the second-order phase transition was observed only for the single $\gamma$-U phase, i.e. alloying with 15 at. % Mo (U-Mo15), while only a broad peak/bump was observed for others. The transition temperature $T_c$ determined from $C(T)$ data for U-Mo15 splat is in a good agreement with that from resistivity. For pure-U splat, only a very weak feature (a small bump) related to the superconducting transition was revealed in the $C(T)$ curve around 0.65 K, i.e. at a

**Table 1. Summary of low-temperature properties of UMo splat samples: resistivity values at 300 K and at 4 K ($\rho_{300\,\text{K}}, \rho_{4\,\text{K}}$), superconducting transition temperatures ($T_c$) defined as the temperature at a half of the jump in the resistivity $\rho(T)$ on/and at the maximum in the specific heat $C(T)$, the width of the superconducting transition in the resistivity ($\Delta T_p = T(\rho_{90\%}) - T(\rho_{10\%})$), critical magnetic fields at zero temperature ($\mu_0 H_c$) estimated by polynomial fits of the experimental data, the respective slopes of the $\chi$ versus $T$ curves at $T_c$ ($\gamma = \mu_0 (dH_c/dT)\gamma_c$).**

| Content (at.%) | $\rho_{300\,\text{K}}$ (µΩ·cm) | $\rho_{4\,\text{K}}$ (µΩ·cm) | $T_c$ (K) | $\Delta T_p$ (K) | $\mu_0 H_c$ (T) | $\gamma = \mu_0 (dH_c/dT)\gamma_c$ (T/K) |
|----------------|-------------------------------|-------------------------------|----------|----------------|----------------|-----------------------------------|
| 0 (pure $\alpha$-U) | 53                           | 14                           | 1.24/0.65 | 0.02           | 0.3            | 0.35                              |
| 3% Mo          | 84                           | 69                           | 0.79/0.65 | 0.09*          | 2.2            | 3.6*                              |
| 6% Mo (UMO6)  | 91                           | 82                           | 1.9/0.90  | 0.60*          | 0.02           | 3.6*                              |
| 10% Mo         | 105                          | 107                          | 0.78/0.65 | 0.78*          | 0.02           | 3.6*                              |
| 11% Mo         | 105                          | 107                          | 1.7/1.25  | 1.9/1.7        | 0.02           | 6.7                              |
| 12% Mo         | 90                           | 98                           | 5.1       | 0.02           | 6.7            | 3.6                              |
| 15% Mo (UMO15) | 89                           | 95                           | 2.1/2.1   | 6.7            | 3.6*           |                                   |
| Pure $\gamma$-U phase |                               |                              |           |                |                |                                   |
much lower temperature than that determined from the resistivity jump (1.24 K). The results suggest that only a small fraction of the sample is really superconducting and that the superconducting fraction forms a 3D network, which is possible e.g. when the superconducting fraction is concentrated at grain boundaries. This finding may support the fact of why there is no superconductivity observed in good-quality U single crystals [8].

We also estimated the height of the specific-heat jump $\Delta C = C_s - C_n$ corresponding to the difference of the specific heat of the superconducting and normal phase. Such a jump is expected from the BCS theory as $\Delta C = 1.43 \gamma_e T_c$, where $\gamma_e$ is the normal-state Sommerfeld coefficient of electronic specific heat and $T_c$ is the superconducting temperature. Using the experimental obtained values for $\gamma_e$ and $T_c$ we calculated the specific-heat jump $\Delta C$ marked by the vertical bars in the figure 4. For U-Mo15, the height of the experimentally observed jump $\Delta C$ is quite close to that expected from the BCS theory [15, 16]. This not only proves that the superconductivity is a bulk effect, but also points to the fact that a weak-coupling may be a good approximation in this case. For other samples, it is more difficult to evaluate the jumps since they are not sharp. However, they are apparently smaller than the calculated ones. Or in other words, for UMo splats with a Mo concentration (<15 at.% Mo), $\Delta C$ exceeds the value expected from the BCS theory. We notice here that for UMo splats with lower Mo concentrations (<11%) the samples contain a certain amount of the $\alpha-$phase, which has a lower $\gamma_e$-coefficient. The bars therefore represent a lower estimation limit. If we took for all such splats the $\gamma_e$-values estimated for well-defined $\gamma-$U phase (U-Mo15), the bars would be, in a higher estimation limit, up to 50% longer. The peak broadening is particularly noticeable for 10% Mo. We cannot be sure whether the broadening is intrinsic or related to the Mo distribution, which was particularly large for this sample. In fact, we observed some sample dependence for 11% Mo, at which concentration several splats were produced. The peak becomes again narrower for 6 and 3% Mo. The fact that they exhibit almost identical $T_c$ ($\approx 0.7$ K

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**Figure 3.** Low-temperature resistivity of three U-Mo splats in applied magnetic fields: a) pure-U (with 0 at. Mo%), b) 6 at.% Mo (U-Mo6) and c) 15 at.% Mo (U-Mo15), revealing respectively $\alpha$-phase, mixed $\alpha + \gamma$ phase and pure $\gamma$ phase. The curves were normalized to respective resistivity values at $T=4$ K.

**Figure 4.** The specific-heat anomalies related to the superconducting phase transition in UMo splats. The vertical bars indicate the calculated values for the specific-heat jump from BCS theory.
determined from $C(T)$ curve) indeed indicates that possible Mo concentration variations do not play much of a role in this range. The fact that it yields about 50% of $1.43\gamma_eT_c$ for 6% Mo and 25% $1.43\gamma_eT_c$ for 3% Mo suggests that the observed superconductivity has to be associated with the bcc phase, the concentration of which progressively decreases with decreasing Mo concentration. We cannot, however, assume that there is a simple phase separation [16].

To see how the $T_c$ anomalies develop we measured low-temperature specific heat in applied magnetic fields, as shown in figure 5. In general, the height of the peaks decreases and they are shifted to low temperatures, following the trend observed already in the resistivity. They also become lower and broader.

We estimated the critical magnetic fields at zero temperature ($\mu_0H_c$) by applying polynomial fits to the experimental data. The temperature dependence of the critical field ($H_c(T)$ curve) for UMo splats determined from electrical resistivity and specific heat data are shown in figure 6. For all investigated UMo splats, neither a quadratic dependence as the temperature approaches 0 K nor a close to linear dependence were observed. In the same figure we also show the fits by second-order polynomial function. For U-Mo15, the critical fields determined from $C(T)$ data lie on the same line determined from the resistivity data. For pure-U splat, the situation is different. Although $T_c$ was determined as 1.24 K from resistivity (as the transition mid-point) and the sample is in a zero-resistance state at $T=1.1$ K, the anomaly in $C(T)$ curve appeared below 1.0 K. The more detailed inspection reveals that the curve in 0 T and 0.6 T has started to deviate between 1.1 and 1.2 K already. The broad transition around 0.65 K can mean that there is actually a broad distribution of $T_c$ values.

The estimated values of the critical slopes at $T_c$ of the $H_c(T)$ curves ($-\mu_0(dH_c/dT)|_{T_c}$) are given in table 1. The values are very similar for different alloys. Thus, we can assume that the upper critical field at $T=0$ is in the range 5–7 T for the $\gamma$-U type of superconductivity. It is very much different for $\alpha$-U superconductivity, where the upper critical field at $T=0$ is about only 0.3 T. The high upper critical field slope at $T_c$ and correspondingly the high upper field of the $\gamma$-U
superconductivity corresponds to materials as A15 superconductors with a strong coupling [17]. However, those A15 superconductors have the $T_c$ values exceeding 10 K, while it is about or below 2 K for UMo alloys. The difference between the standard A15 superconductors and $\gamma$-U alloys may be related to the disorder.

4. Concluding remarks

By using the ultrafast cooling with the cooling rate of $10^6$ K s$^{-1}$, we could reduce the necessary Mo amount for stabilizing the single $\gamma$-U phase with only 13 at.% Mo. A new ingredient is a robust BCS-type superconductivity culminating for $\gamma$-U alloy (U-Mo15) with $T_c$ exceeding 2.1 K and upper critical field is larger than 5 T. It might be in analogy with that of U$_6$Fe [17]. In contrast, the superconductivity in the pure $\alpha$-U is not a real bulk effect, although a clear resistivity jump was revealed at 1.24 K. Our results indicate that the $\alpha$-U and $\gamma$-U superconductivity are qualitatively different, despite the fact that there is no substantial difference in the superconducting phase temperature $T_c$.

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