

Contribution to the uranium–gallium phase diagram

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Abstract

Uranium-rich gallium alloys were studied by metallography, electron microscopy, X-ray diffraction and differential thermal analysis. Gallium additions allow retaining metastable β -uranium alloys at ambient temperature. The solubility of Ga in the high temperature uranium phases was determined by WDS, reaches 8 at.% at 800 °C in U_γ and 1.2 at.%, in U_β at 720 °C. The presence of the Ga_5U_3 compound, structure type Pd_5Pu_3 , was confirmed.

Moderate mechanical stresses at room temperature promote the transformation of the metastable U_β alloys into $U_{\alpha'}$ by a shear-like transformation. The latter is a Ga-containing metastable variant of the room temperature equilibrium uranium allotrope. The metastable structure ultimately reverts to the equilibrium U_α and releases excess Ga by precipitation of the U_3Ga_5 compound in the form of thin platelets.

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1. Introduction

The general features of the uranium–gallium phase diagram, including the presence of three intermetallic compounds, namely, UGa_3 , UGa_2 and U_2Ga_3 were determined by Buschow [1]. No data was reported on the uranium-rich side of the binary diagram and, in particular, none regarding the solubility of Ga in the three allotropes of uranium metal. Several transition metals, e.g. Ti, Mo, Nb, have extended solubility in the high temperature bcc U_γ phase. In some instances the latter high temperature phase may be retained as a metastable solid solution at ambient temperature, opening the way to a variety of heat treatments that involve controlled phase transformations and/or aging that are actually taken advantage of, in order to manufacture high strength alloys for a variety of applications.

Dayan et al. [2] reported that the addition of 1.5 at.% Ga and cooling from the U_β or the U_γ phase temperature domains allow the retention at room temperature of the tetragonal U_β structure. At the ambient, U_β is metastable and undergoes a shear-like

isothermal transformation into α' , a distorted U_α -like structure [3]. The higher the gallium content of the initial alloy, the more sluggish the martensitic transformation into to the α' structure. The α' -U structure, with the same composition as its mother β -U solid solution, decomposes after an aging treatment into a two-phase structure consisting of virtually Ga-free U_α and the intermetallic compound U_3Ga_5 [3]. The presence of this latter compound, U_3Ga_5 had not been reported in the initial study of the phase diagram [1], in which it had been mistakenly identified as U_2Ga_3 .

The solubility of Ga in the low temperature U_α structure is very limited. According to the later studies of Dayan et al. [2], it is substantially higher in the two high temperature uranium phases. The intermediate temperature U_β structure can be retained at ambient temperature by Ga additions and quenching at a moderate rate. In contrast, the high temperature U_γ phase transforms even at a high cooling rate into the U_β -structure and only the latter can be retained at ambient temperature.

The microstructures at ambient temperature of the structures formed at elevated temperature in the different uranium phases reflect both the solubility of Ga in these phases and the effect of the cooling regimes down to ambient temperature. The objective of the present study was to take advantage of these features of the U(Ga) alloys in order to determine the solubility of Ga in the

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high temperature uranium phases and correlate with the resulting microstructures.

2. Experimental procedures

The uranium gallium alloys were prepared by arc-casting under a purified argon atmosphere. The starting uranium metal contained 300 ppm impurities (30 ppm carbon) and the gallium metal was 99.95% pure. The molten alloys were cast into water cooled split copper mold in the form of 9 mm in diameter, 45 mm high cylindrical rods. The cast rods were wrapped in thin Ta foils and homogenized under vacuum in quartz tubes at 1000 °C for 7 days and water quenched to room temperature. Parts of each sample were used for chemical analysis for determination of the gallium content. The samples were electropolished at 25 V for 30 s in a solution consisting of 50 gr CrO₃, 60 ml H₂O, and 420 ml CH₃COOH. The morphology was studied by optical and scanning electron microscopy. Wavelength dispersive spectrometry (WDS) and conventional correction procedures were used to determine the composition of the different phases. The structure of the intermetallic compounds was determined by powder X-ray diffraction using the Rietveld analysis. Differential thermal analysis (DTA) was also used to determine the temperature of the phase transformations in the uranium rich alloys.

3. Results and discussion

3.1. The solubility limits of Ga in U_γ and U_β

The solubility limits of Ga in the U_γ and U_β phases were determined by WDS analysis of the Ga concentration in samples quenched from different temperatures in the γ- and the β-phase, respectively, to room temperature. To ensure the reliability of the WDS analysis after the ZAF correction, a calibration curve was constructed using the results obtained from analysis of the composition of the single phase U₃Ga₅ compound. The results are summarized in Table 1 and in Fig. 1. The latter also includes results derived from the DTA curves, which are shown in Fig. 2. The lattice parameters of the metastable U_β(Ga) alloys, determined at room temperature, are shown in Fig. 3. It is noteworthy that alloys that had been annealed in the U_γ temperature range retain the U_β structure, (by quenching to room temperature) with 8 at.% Ga, whereas in alloys that had been annealed to begin with within the U_β temperature, the Ga content after quenching did not exceed 1.2 at.%. The solubility limit values of Ga in the U_γ are given in Table 1, and are believed to be equilibrium or close to equilibrium values. It is highly unlikely that faster quenching rates than the one that was used would have changed the Ga concentration within the U_β grains. The solubility of gallium in the different uranium phases decreases with decreasing temperature. The decrease is continuous within the temperature range of each allotropic phase and discontinuous at the phase transfor-

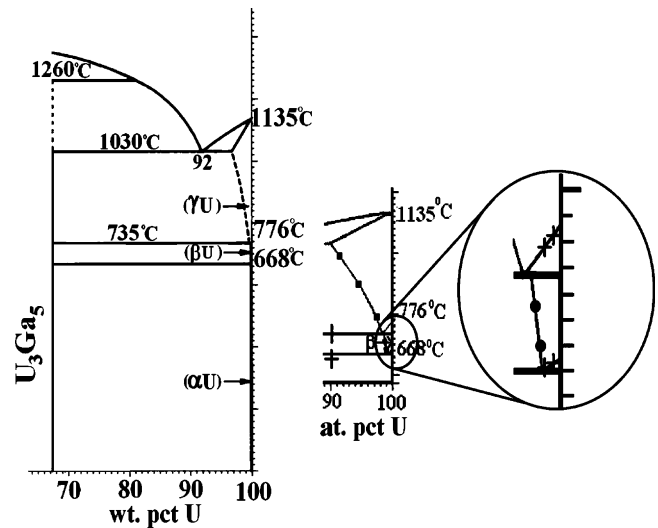


Fig. 1. Uranium-rich side of the U–Ga diagram. The right-side insert shows the high U concentration region in greater details. Crosses stand for data obtained by DTA and the dots for the WDS results in the quenched metastable U_β alloys.

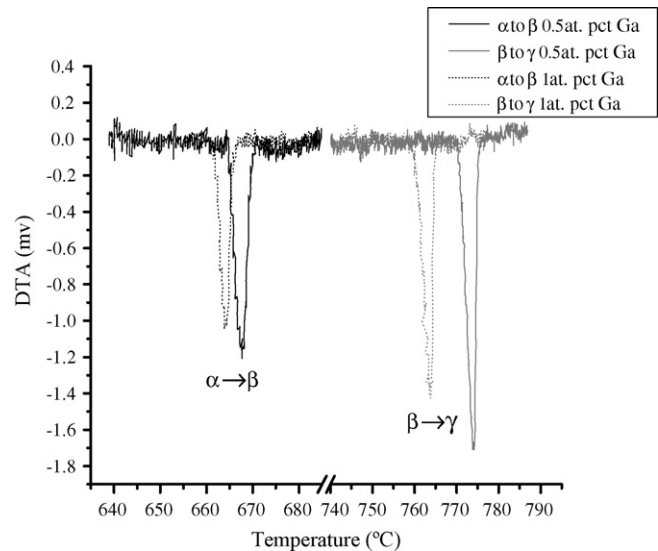


Fig. 2. Differential thermal analysis curves obtained in the course of heating the U(Ga) alloys.

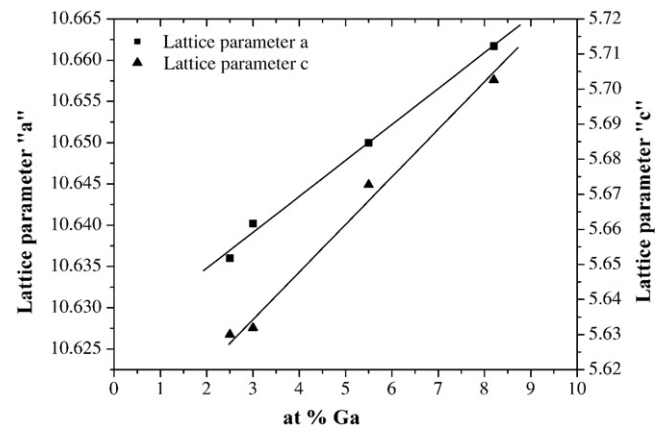


Fig. 3. Room temperature lattice parameters of the metastable U(Ga) alloys that had been quenched from various temperatures in the U_γ and the U_β phase. The Ga concentration had been determined in the quenched alloys by WDS analysis.

Table 1
Solubility limit of Ga in U_γ and U_β as determined at ambient temperature by WDS in metastable U_β(Ga) alloys

Matrix	Temperature (°C)	Solubility limit (at.%)
U-γ	1000	8.2 ± 0.1
	900	5.6 ± 0.2
	800	2.9 ± 0.4
U-β	710	1.2 ± 0.2
	680	1.1 ± 0.4

Table 2

The eutectoid Ga concentration in the uranium-rich Ga alloys

Eutectoid reactions at cooling	Ga concentration (at.%)
$U_{\gamma}(\text{Ga}) \rightarrow U_{\beta}(\text{Ga}) + U_3\text{Ga}_5$	1.5 ± 0.02
$U_{\beta}(\text{Ga}) \rightarrow U_{\alpha}(\text{Ga}) + U_3\text{Ga}_5$	1.19 ± 0.02

mation temperatures. The eutectoid concentrations for the two, $U_{\gamma} \rightarrow U_{\beta} + U_3\text{Ga}_5$ and $U_{\beta} \rightarrow U_{\alpha} + U_3\text{Ga}_5$ reactions, shown in Table 2, were calculated on the basis of the DTA results shown in Fig. 2, the Ga concentration values determined by WDS and by using the two eutectoid temperatures reported in [1].

3.2. The morphology of the uranium-rich Ga alloys

With decreasing temperature, excess gallium is expelled from the uranium matrix and precipitates as the intermetallic compound $U_3\text{Ga}_5$ [4]. The distribution and the morphology of the precipitates within the solvent matrix are determined by several factors. These factors are the temperature versus time relation in the course of the precipitation process, the diffusivities of gallium in the three uranium phases and other surface and strain energy related factors. In uranium alloys with relatively large Ga

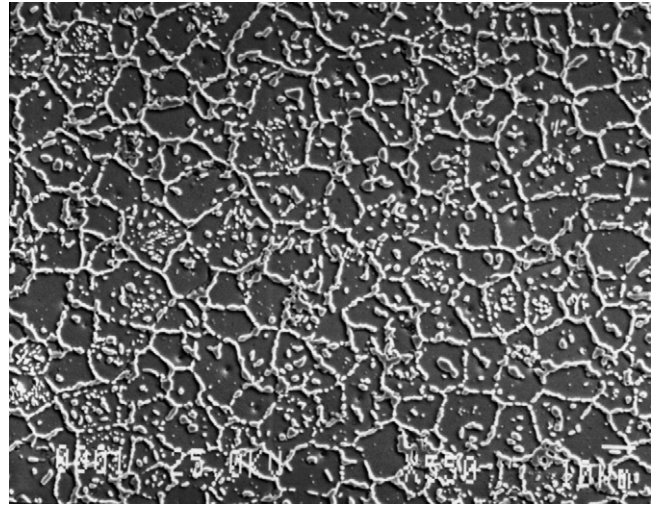


Fig. 5. SEM micrograph of a U-15 at.% Ga sample, after annealing at 710 °C. The structure consists of the metastable U_{β} matrix and $U_3\text{Ga}_5$ precipitates. Some of the latter delineate the grain boundaries and were formed during the passage through the temperature range above the U_{β} phase, others precipitated within the grains during the annealing stage in the U_{β} temperature range.

content (>10 at.%), after a γ -phase anneal, excess Ga above its solubility limit precipitates at the grain boundaries as the $U_3\text{Ga}_5$ phase (Fig. 4).

With the greatly reduced solubility of Ga in the β -phase, as compared to that in the γ -phase, after annealing in the β -phase temperature range, additional excess Ga precipitates within the U_{β} matrix. In contrast to samples that had been annealed in the U_{γ} -phase, excess gallium at the lower temperature of the annealing treatment lacks the mobility to diffuse to grain boundaries and precipitates within the β -phase matrix, as shown in Fig. 5.

The maximum Ga content in U_{β} at 710 °C stands at 1.2 at%. This apparently is still in excess of the highest allowed Ga content in U_{α} . Upon cooling slowly to the high U_{α} range at

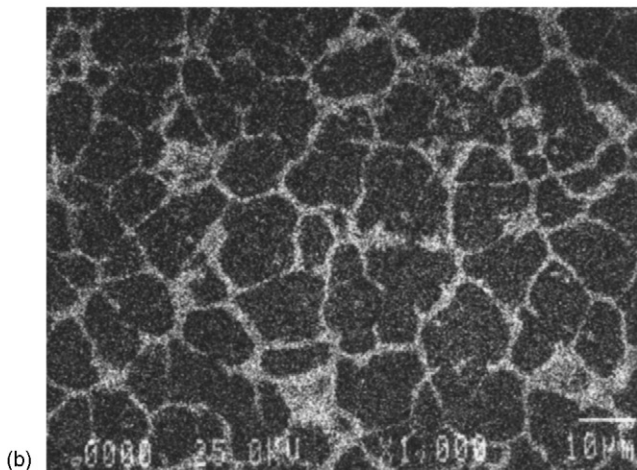
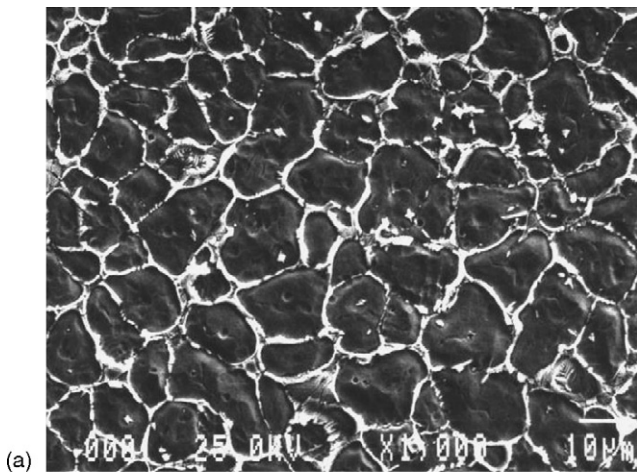


Fig. 4. (a) SEM secondary electron micrograph, and (b) Ga- K_{α} X-ray mapping of a 30 at.% Ga sample after cooling in the arc furnace.

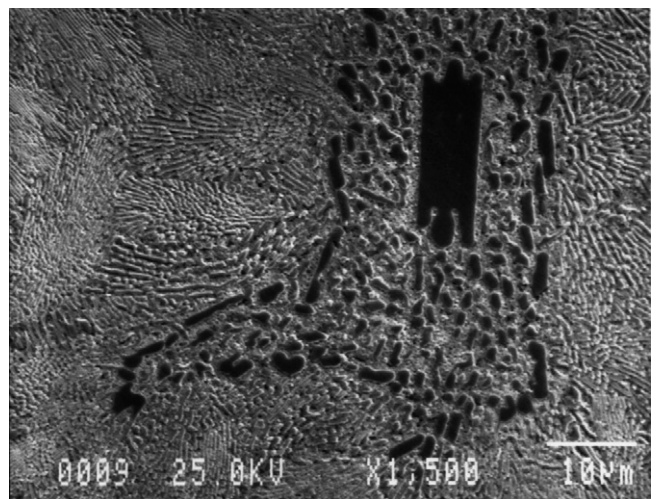


Fig. 6. SEM micrograph of a U-3 at.% Ga sample, after annealing at 400 °C. The matrix is almost a fully eutectoid $U_{\alpha} + U_3\text{Ga}_5$ structure; the dark islands are $U_3\text{Ga}_5$ precipitates that appeared during cooling through the U_{β} and U_{γ} temperature range. The eutectoid microstructure was formed when the sample was slowly cooled through the $U_{\beta}(\text{Ga}) \rightarrow U_{\alpha}(\text{Ga}) + U_3\text{Ga}_5$ eutectoid isotherm.

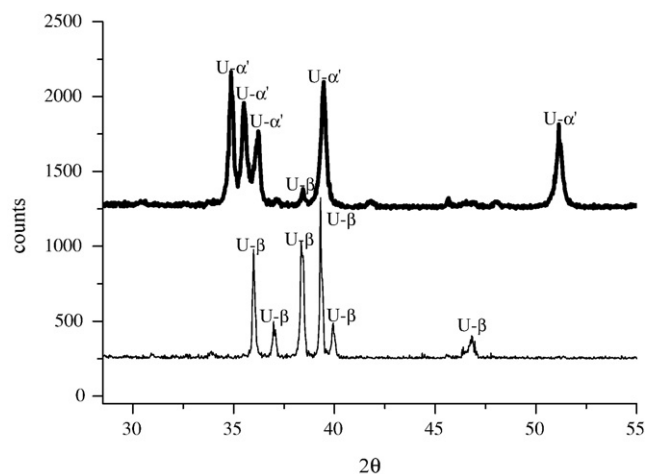


Fig. 7. X-ray diffractograms of a U-1.5 at.% Ga alloy after a quench to room temperature. After electrolytic polishing, a metastable U_{β} structure (lower spectrum), and after mechanical polishing, a metastable $U_{\alpha'}$ structure (upper spectrum), are present.

400 °C, the sample undergoes an additional eutectoid reaction $U_{\beta}(\text{Ga}) \rightarrow U_{\alpha}(\text{Ga}) + U_3\text{Ga}_5$, and excess Ga as $U_3\text{Ga}_5$ appears in the lamellae of the microstructure (along with some pre-eutectoid $U_3\text{Ga}_5$ that precipitated while the sample was still was in the β -phase temperature range, Fig. 6).

3.3. Strain induced transformation of the metastable $U_{\beta}(\text{Ga})$ structure to $U_{\alpha'}(\text{Ga})$

Metastable $U_{\beta}(\text{Ga})$ decomposes into $U_{\alpha}(\text{Ga})$ and $U_3\text{Ga}_5$ precipitates after annealing in the upper U_{α} temperature range. Mechanical strains, e.g. mechanical polishing at room temperature may also cause the transformation of the metastable $U_{\beta}(\text{Ga})$ structure, by a shear like mechanism that takes place at room temperature into α' -uranium (Fig. 7) [3,4]. The latter is a distorted variant of the U_{α} uranium structure to which it ultimately reverts by releasing excess Ga *via* precipitation of the $U_3\text{Ga}_5$ compound in the form of thin platelets. The uranium-rich U(Ga) alloys and the plutonium-rich Pu(Ga) alloys display, with respect to the shear like transformation that takes place in the metastable Pu_8 and the U_{β} structures, some similar features. Unlike the Pu alloys, however, the decomposition of the metastable U solid solution does not require sub-ambient temperatures.

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