Phase Transformations in a Uranium-Zirconium Alloy containing 2 weight per cent Zirconium

G. Lagerberg
PHASE TRANSFORMATIONS IN A URANIUM - ZIRCONIUM
ALLOY CONTAINING 2 WEIGHT PER CENT ZIRCONIUM.

G. Lagerberg

Summary.

The phase transformations in a uranium-zirconium alloy containing 2 weight percent zirconium have been examined metallographically after heat treatments involving isothermal transformation of γ and cooling from the γ-range at different rates. Transformations on heating and cooling have also been studied in uranium-zirconium alloys with 0.5, 2 and 5 weight per cent zirconium by means of differential thermal analysis. The results are compatible with the phase diagram given by Howlett and Knapton (1).

On quenching from the γ-range the γ phase transforms martensitically to supersaturated α, the $M_S$ temperature being about 490 °C. During isothermal transformation of γ in the temperature range 735 to 700 °C β-phase is precipitated as Widmanstätten plates and the equilibrium structure consists of β and γ₁. Below 700 °C γ transforms completely to Widmanstätten plates which consist of β above 660 °C and of α at lower temperatures. Secondary phases, γ₂ above 610 °C and δ below this temperature, are precipitated from the initially supersaturated Widmanstätten plates during the isothermal treatments. At and slightly below 700 °C the cooperative growth of β and γ₂ is observed. The results of isothermal transformation are summarized in a TTT-diagram.

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Phase transformations in a uranium-zirconium alloy containing 2 weight percent zirconium.

1. Introduction.

The efficient use of metallic uranium as a nuclear reactor fuel is limited due to dimensional changes occurring as a result of irradiation and thermal cycling at elevated temperatures. In order to minimize these effects as far as possible a fine grained and texture-less metal is desired. Such a condition is more easily obtained if the uranium is alloyed. Alloying might also increase the resistance to plastic flow which in turn will increase the critical temperature for swelling due to the formation of fission gas bubbles. From the point of view of neutron economy zirconium with its low absorption cross section for thermal neutrons is one of the very few alloying elements that could be considered for these purposes in a reactor based on natural uranium. An optimum addition seems to be about 2 weight percent (w/o). The behaviour of this alloy as a reactor fuel has also been extensively studied and is described in several reports from Argonne National Laboratory, Nuclear Metals Inc. and Battelle Memorial Institute in USA and from the Atomic Energy of Canada Ltd.

The binary phase diagram uranium-zirconium has been studied by several investigators. Fig. 1 shows the diagram according to Howlett and Knapton (1) which was based on a re-investigation of earlier work by Summers-Smith (2). The latter author did not include the intermediate phase here designated δ. This phase has sometimes been assumed to be metastable but is now well established as a stable phase (3, 4). On the low zirconium side of the diagram disagreement exists about the extension of the α phase field. Thus according to the diagram due to Howlett and Knapton β transforms eutectoidally to α and γ₂ at 662 °C. However, Saller, Rough and Bauer (5) assume a peritectoid reaction $\beta + \gamma_1 \rightarrow \alpha$ at 700 °C, as based on quantitative metallographic analysis and on high temperature X-ray diffraction studies (6). Their version of the phase diagram, shown in fig. 2, is supported by investigations by Philibert and Adda (7) and by Bellot, Henry and Cabane (8) using X-ray microanalysis and differential
thermal analysis respectively. However, Chiswick et al (9) arrive at similar results as Howlett and Knapton. Neither of these authors specify their methods of investigation.

Studies of transformation behaviour have been reported for uranium-zirconium alloys with rather high zirconium contents (10, 11) but no systematic investigation of the transformations at low zirconium contents seems to have been published. The present investigation deals with the transformation behaviour in a uranium-2 w/o-zirconium alloy. The main part consists of a metallographic study of the isothermal transformation of γ in the temperature region 720 to 100 °C from which a time-temperature-transformation (TTT) diagram is derived. Supplementary studies of transformation during heating and cooling were carried out for alloys with zirconium contents ranging from 0 to 5 w/o by means of differential thermal analysis (DTA).

The results support the phase diagram proposed by Howlett and Knapton.

2. Experimental methods.

Test materials

The uranium-2 w/o-zirconium alloy was produced from calcium reduced uranium metal and zirconium sponge. The alloy was first melted under vacuum in a graphite crucible with a double coating of magnesium zirconate and thoria to prevent excessive carbon pick up. The melt was cast under vacuum in similarly lined graphite molds into ingots, 38 mm in diameter and 500 mm in length. Two such ingots were welded together and melted as a consumable electrode in a vacuum arc furnace with a water cooled copper hearth. The resulting ingot with a diameter of 80 mm was divided into four 90° sectors one of which was machined to a bar with a 30 mm diameter. This bar was hot rolled at 650 °C to a diameter of 12 mm. Chemical analysis yielded the following results.
Under the microscope specimens from the top end showed much carbides whereas the bottom end was relatively free from these inclusions. It is believed that the carbides segregated towards the top end of the ingot during arc melting because of their low density as compared to that of the metal. UC and ZrC are isomorphous and have been shown to be mutually soluble at 1200 °C (12). Hence it is likely that the carbide phase observed is (U, Zr) C in accordance with the fact that both carbon and zirconium are enriched at the top end. Also oxygen and nitrogen are enriched at this end and it is not unlikely that they are at least partially dissolved in the carbide phase (13). It was found that the high carbide content was confined to a short piece of the top end of the bar. The remainder of it exhibited the low carbide content corresponding to the analysis figures for the middle and bottom end of the bar and was used as test material.

For the DTA-measurements two additional alloys with 0.5 and 5 w/o zirconium were prepared by arc melting. For the low zirconium alloy metal from the 2 w/o alloy was diluted with technically pure uranium and for the high zirconium content such uranium was melted together with iodide zirconium. Melting was carried out in argon at low pressure on a water cooled copper hearth and was repeated six times. It was followed by annealing in the arc for 15 minutes at a temperature slightly below solidus. The melts weighed about 20 g and their compositions were calculated from the known weights of the starting materials assuming complete recovery. The technically pure uranium analyzed 60 ppm of carbon as chief impurity.

<table>
<thead>
<tr>
<th>12 mm bar</th>
<th>Zr w/o</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top end</td>
<td>2.4</td>
<td>700</td>
<td>150</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>1.9</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Bottom end</td>
<td>1.8</td>
<td>85</td>
<td>15</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>
Heat treatment

The specimens used for heat treatment were half moon shaped disks obtained by cutting 3 mm thick slices normal to the rolling direction of the uranium-2 w/o zirconium bar and dividing these along a diameter. A small hole was drilled at the edge of the specimen so that it could be attached to a stainless steel wire for the rapid manipulation during heat treatment. For short times of isothermal heat treatment 0.5 mm thick specimens were used to ensure rapid attainment of the transformation temperature.

For the isothermal transformation treatments specimens were solution treated at 900 °C for 15 minutes in a tube furnace with argon atmosphere. They were then rapidly transferred to the transformation temperature at which they were held for various lengths of time. The transformation was interrupted by quenching in a solution of 10% sodium hydroxide in water. For transformation temperatures between 720 and 575 °C a salt bath was used consisting of a mixture of CaCl₂, NaCl and KCl (Durferrit GS 430) in a steel crucible. Before use the bath was deoxidized with silicon. For intermediate temperatures down to 200 °C transformations were carried out in a lead-tin bath and at 100 °C in boiling water.

In general the specimens started to corrode heavily after some hours in the salt bath or in the lead-tin bath. Hence specimens intended for long transformation times (8 hours and more) were sealed into evacuated quartz capsules and rapidly transferred from a tube furnace at the solution temperature to another tube furnace at the transformation temperature. Subsequently the specimen was quenched by breaking the capsule under the sodium hydroxide solution. This transformation treatment proved satisfactory for the higher temperatures. Below about 660 °C the cooling from the solution temperature was too slow to prevent partial transformation before the transformation temperature was reached, however. Lengthy isothermal treatments at these temperatures were therefore carried out also by first transforming the bare specimen in a salt or lead bath until all γ had transformed, quench, and
then continue the treatment in a tube furnace with the specimen sealed in a quartz capsule. Except for the transformation products formed above the transformation temperature in the first method, the two methods yielded the same structures. The second method was used at 575 °C and lower temperatures exclusively.

Heat treatments involving furnace cooling and air cooling were performed with the specimens sealed in evacuated quartz capsules. To reduce contamination from quartz capsules specimens were sometimes wrapped in zirconium foil.

**Metallographic preparation**

After mounting the specimen a section parallel to the rolling direction was prepared for metallographic examination. The surface was wet ground on successively finer silicon carbide papers down to paper no 320. It was then polished electrolytically according to Mott and Haines (14) using an electrolyte of 10 g pyrophosphoric acid, 10 g chromic oxide, 40 cc orthophosphoric acid, 100 cc sulphuric acid and 100 cc distilled water. The voltage was 10 V, the current density 0.25 A/cm² and the time of polishing about 1 minute. During polishing the specimen was gently rubbed with a piece of cotton to remove the reaction products formed. The resulting specimen surface exhibited a slight tarnish which was removed by a light mechanical polish on alumina. In this condition the morphology of the α-uranium crystals could be studied in polarized light.

A large number of the etching methods recommended in the literature for uranium-zirconium alloys were tried. Most of these yielded poor results mainly because of heavy oxidation. The method finally adopted was an electrolyte used for uranium-molybdenum alloys by Hills et al (15). The composition of the electrolyte was 10 g citric acid, 10 g nitric acid and 90 cc distilled water. The voltage was 3 V, the current density 0.2 A/cm² and the etching time 5 to 15 seconds. The best etching results were obtained if the specimen had been
polished as described above. A specimen that had been polished mechanically on diamond dust and on alumina was in general considerably tarnished during etching.

Cathodic bombardment etching according to Armstrong, Madsen and Sykes (16) was tried on mechanically polished specimens. Except for a few cases in which finely dispersed structures were clearly disclosed the results were not satisfactory.

3. Experimental results.

3.1. Isothermal transformation of \( \gamma \)

Quenching from the \( \gamma \)-range

Quenching from the \( \gamma \)-range results in a structure of lens shaped plates with irregular boundaries in an acicular matrix consisting of fine plates or needles as is illustrated in fig. 3 for a specimen quenched from 900 °C. Fig. 3 a shows the structure after etching in citric acid and fig. 3 b the same area in the unetched condition using polarized light. A previous \( \gamma \)-grain boundary is visible as a border line limiting the extension of a group of large plates. X-ray diffraction of the polished surface using a Norelco diffractometer with Cu Kα radiation yielded a \( \alpha \)-uranium pattern corresponding to a slightly expanded unit cell. It is believed that the large plates as well as the fine plates or needles of the matrix are formed by the martensitic transformation of \( \gamma \) to \( \alpha \) as will be discussed below. The \( \alpha \) formed in this way \( \gamma \) will probably to a large extent inherit the zirconium content of the \( \gamma \)-phase and will thus become supersaturated with zirconium. This type of \( \alpha \) will be termed \( \alpha_1 \) in the following account in order to distinguish it from the \( \alpha \) formed under conditions permitting its composition to approach equilibrium more closely.

*) The notation \( \gamma \) in the following account generally refers to a composition corresponding to \( \gamma_1 \) in the phase diagrams in figs. 1 and 2.
Transformation above 700°C

After solution treatment at 900°C and subsequent isothermal treatment at 720°C the α¹-structure is obtained upon quenching for holding periods up to about 15 minutes at the latter temperature. On continued holding a bright etching phase appears in the α¹-matrix as illustrated in figs. 4, 5a and 6. The bright phase first forms as tiny islands at previous γ-grain boundaries and as Widmanstätten plates within the γ-grains (fig. 4). After some time the γ-grains are more or less enveloped by an irregularly shaped rim of this phase and numerous Widmanstätten plates have formed in the interior of the grains (fig. 5a). Initially the plates exhibit straight and often parallel edges but soon become more rounded as a result of spheroidisation. The latter process will also eventually lead to the breaking up of the grain boundary rims and bring about an equilibrium structure consisting of rounded islands of bright phase in a matrix of α¹ (fig. 6). At 710°C the transformation proceeds similarly but the amount of bright phase formed at equilibrium is increased.

Judging from the phase diagrams published, e.g., those in figs. 1 and 2, the bright phase formed in the temperature region considered is β. However, as found from X-ray results the β is not retained but transforms to α upon quenching. This α is only moderately supersaturated on zirconium owing to the restricted solubility of zirconium in β. Fig. 5b shows the same specimen area as fig. 5a but in the unetched condition under polarized light. The islands of bright phase of fig. 5a appear as units of α with many subgrains. This means that the β-units have transformed to α without interference from the transformation of γ to α¹ of the matrix. This is a general feature for the bright phase formed in this temperature region.

Transformation at 700°C

On transformation at 700°C the bright phase starts to form as plates of Widmanstätten character in which ridges or rows of dots of a secondary precipitate in the length direction of the plates are observed.
In between these plates a pearlite like product of the same phases develops. Both structure types are shown in fig. 7. Within 10 minutes the \( \gamma \)-phase has transformed completely. Because of the proximity to the eutectoid temperature longer times of heat treatment resulted in inconsistent structures indicating that the specimen had spent unknown proportions of the time in different phase regions. Hence, for these times studies of structural changes were not attempted.

**Transformation in the region 690 to 500 °C.**

As observed under the microscope the isothermal transformation of \( \gamma \) in the region 690 to 500 °C seems to follow one and the same general pattern. The typical sequence of changes is illustrated for the transformation at 690 °C in figs. 8 to 11. After about 15 seconds at this temperature narrow Widmanstätten plates which after etching stand in relief over the \( \alpha \)-matrix start to appear (fig. 8). They seem to nucleate rather uniformly throughout the matrix with a slight preference for nucleation sites at inclusions and \( \gamma \)-grain boundaries. The etched surface of the plates has a wrinkled appearance giving the impression of a system of densely spaced ridges parallel to the longitudinal directions of the plates. The Widmanstätten plates grow rapidly and soon consume the \( \gamma \)-matrix entirely as illustrated by fig. 9a. The same Widmanstätten pattern is also observed in the unetched condition in polarized light (fig. 9b). At this stage of transformation the ridges are more marked and on further holding they partially transform into rows of dots (fig. 10a). Obviously a secondary phase is precipitated from the initially supersaturated Widmanstätten plates. When the precipitation reaction appears to be about completed the Widmanstätten plates merge together to form a smooth and uniform background (fig. 10a) which is probably a result of grain growth or recrystallization as is obvious from fig. 10b. In the following account the process will be referred to as recrystallization. On prolonged holding the precipitate undergoes coalescence to rounded particles and plates (fig. 11).

At decreasing temperatures the Widmanstätten plates formed on isothermal transformation become successively finer. The initial
precipitation possibly proceeds somewhat more rapidly when decreasing
the temperature from 690 °C to 650 °C as the surface of the plates after
short times of treatment appears more mottled the lower the tempera-
ture in this region. At still lower temperatures no accurate observations
of the initial precipitation has been made because the structures are so
finely dispersed. The lower the temperature the longer are the times
required until a distinct precipitate is observed and until the recrystal-
lization commences. Below about 650 °C the preference for nucleation
of Widmanstätten plates at grain boundaries is increased. This is no-
ticeable from the fact that γ-grain boundaries are often decorated by
fringes of parallell plates of a uniform lattice orientation growing into
the grain as shown in figs. 12 a and b. The finer scale of the reaction
products at lower temperatures is illustrated in figs. 12 and 13. The
transformation proceeds very rapidly below about 600 °C as no remnants
of γ are observed after periods as short as 2 seconds.

From the microscopical features of the Widmanstätten plates
formed in the temperature region considered no conclusions can be
drawn as to whether they are formed as β-plates which subsequently
transform to α on quenching or form directly as α-plates. X-ray
diffraction indicated the α-uranium structure in all instances the unit
 cell being slightly expanded at the beginning of transformation and
 gradually approaching the normal lattice parameters during the course
 of transformation. However, as inferred from the DTA-results pre-
sented below the plates are β above about 660 °C and α below this
temperature. This means that β-plates on quenching transform indi-
vidually to more or less perfect α-plates as is evident from figs. 9a
and 9b. The decrease in lattice parameter as a result of isothermal
treatment probably reflects the rejection of zirconium from the initially
supersaturated transformation product.

The changes taking place during isothermal treatment for periods
up to 2 hours were also followed by measuring the hardness of quenched
specimens (fig. 14). As would be expected the precipitation of a secon-
dary phase, and at 690 and 675 °C, also the recrystallization eventually
leads to a softening. The curve at 575 °C exhibits a typical precipitation
12.

hardening peak. The decrease in initial hardness with temperature in the region from 690 to 650 °C might be a consequence of a corresponding acceleration in the initial precipitation reaction. The increase in initial hardness when decreasing the temperature below 650 °C is probably a result of a finer dispersion of the reaction products.

**Transformation below 500 °C.**

After short transformation times in the temperature region below 500 °C large lens shaped plates appear in a finely accicular matrix as is illustrated for transformation at 350 °C in fig. 15. The size and shape of the large plates is independent of transformation temperature and time. However, the number of these plates increases the lower the transformation temperature. Thus at 475 °C only a few single plates are observed whereas at 100 °C plates appear rather densely as shown in fig. 16. Still more large plates are formed upon quenching to room temperature as is evident from fig. 3 a. Obviously the large plates are the α³ phase formed by the martensitic transformation of γ. The Mₘₙ temperature for this reaction lies between 500 and 475 °C.

The acicular matrix surrounding the α³ plates forms in a manner analogous to that described for the temperature region above 500 °C. Thus the part of the γ phase, that on passing the Mₘₙ temperature does not form α³, rapidly transforms by the formation of fine plates which are probably supersaturated with zirconium. The nucleation of such plates at γ-grain boundaries is frequently observed (fig. 15). On prolonged holding fine particles of a secondary phase are precipitated from the fine supersaturated plates and at least at the higher temperatures a transition from a large number of individual crystals to a coarser crystalline structure is observed under polarized light. However, these reactions proceed very sluggishly and they have not been studied in detail.

Precipitation of a secondary phase within the α³ plates on prolonged holding at the transformation temperature has also been observed.
The transformation diagram

Based on the observed structures of transformed specimens the TTT-diagram of fig. 17 has been constructed. The solid curves denote the beginning and end of $\gamma$-transformation. The accurate drawing of these curves was to some extent aided by judging visually the degree of transformation. In their uncertain extensions the curves are dashed. A dashed curve also denotes the start of recrystallization of the Widmanstätten matrix.

The marked discontinuities at about 660 °C in the curves for the beginning and end of $\gamma$-transformation indicate a change in the transformation mechanism at that temperature. This result combined with the fact that the curve for the start of transformation seems to be continuous from 660 °C and upwards in the ($\delta + \gamma$)-region strongly suggest the type of phase diagram proposed by Howlett and Knapton (1), fig. 1. The discontinuity at about 610 °C in the curve for the end of $\gamma$-transformation might possibly reflect the horizontal for the peritectoid reaction $\gamma_2 + \alpha \rightarrow \delta$ in this phase diagram, which is also qualitatively supported by the DTA-measurements presented below. However, a more likely explanation will be given in the discussion. The $M_s$ temperature for the martensitic $\gamma \rightarrow \alpha^+$ reaction has been placed at 490 °C.

In accordance with the phase diagram the secondary phases observed are assumed to be $\gamma_2$ above and $\delta$ below about 610 °C.

The existence ranges for the various phases that are indicated in the TTT-diagram have been inferred from the phase diagram of fig. 1 and the present observations.

3.2. Transformation structures obtained on cooling from the $\gamma$-range

As an application to the TTT-diagram transformation structures were studied after cooling from the $\gamma$-range at different rates.
Oil quenching from 900 °C yielded a structure similar to that observed on quenching in boiling water, fig. 16. Hence, at this cooling rate the γ transforms below the M'_s-temperature (about 490 °C) by the martensitic γ→α^1 reaction and possibly also to a minor extent by the direct formation of supersaturated acicular α as previously outlined. The distinction between these two reactions will be further discussed.

Cooling in air from the same temperature results in a Widmanstätten structure typical of that formed on isothermal transformation between 700 and 650 °C as illustrated in fig. 9 a. The same plate structure is also observed in polarized light. It is concluded that the γ transforms to β-plates which in turn transform individually to α-plates.

Furnace cooling at a rate of about 2 °C per minute results in a complex structure the formation of which was studied by cooling specimens from 800 °C to successively lower temperatures from which they were quenched. Slightly above 700 °C β starts to form as a few rounded islands that rapidly grow in size while retaining smooth boundaries towards the γ-matrix. After cooling to 690 °C the β-island have grown further and in some places their boundaries appear ragged because of the outgrowth of fringes of parallel Widmanstätten plates from the smooth β as shown in fig. 18. A secondary precipitate is observed as dots or ridges at the boundaries of these plates. At 680 °C about 40 % of the specimen area is occupied by untransformed γ. The β-islands seem to have grown exclusively by extending Widmanstätten fringes but isolated plates of β also occur within the γ-matrix as shown in fig. 19. Slightly below 670 °C the last remnants of γ are transformed. The structure now consists of smooth patches (β formed above and slightly below 700 °C) in a matrix of Widmanstätten plates of varying size. The larger plates are those which originally formed as isolated units in the γ-matrix. The secondary phase at the plate boundaries becomes more distinct on further cooling but otherwise no spectacular changes are observed.

Fig. 20 shows the Widmanstätten pattern outlined by the precipitate after cooling to room temperature. Recrystallization as observed during isothermal transformation is almost completed at the end of γ transformation (slightly below 670 °C) and the transformation of β to α must be assumed to take place somewhere below 650 °C (cf DTA-measurements).
3.3. Grain size of the α-phase.

Since one of the main objectives for alloying uranium metal is to reduce its grain size it is of interest to study the effect of an addition of 2 w/o zirconium in this respect. Grain size in α-uranium is difficult to estimate because of the abundance of subgrains which makes measurements of grain diameters in polarized light very subjective. With this reservation the following figures may be quoted for some of the heat treatments in the present investigation.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Average grain diameter in microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal transformation</td>
<td></td>
</tr>
<tr>
<td>at 690 °C for 8 hr (fully recrystallized)</td>
<td>50 - 100</td>
</tr>
<tr>
<td>Isothermal transformation</td>
<td></td>
</tr>
<tr>
<td>at 575 °C for 144 hr (partly Widmanstätten)</td>
<td>20 - 50</td>
</tr>
<tr>
<td>Furnace cooling from</td>
<td></td>
</tr>
<tr>
<td>800 °C at a rate of 2 °C/min. (fully recrystallized)</td>
<td>80</td>
</tr>
<tr>
<td>Air cooling from</td>
<td></td>
</tr>
<tr>
<td>900 °C (Widmanstätten)</td>
<td>10 - 30</td>
</tr>
</tbody>
</table>

These figures should be compared to a grain diameter of 200 microns which about corresponds to the smallest grain size which could be considered as reasonably stable in the α-range for technically pure uranium.

3.4. Differential thermal analysis (DTA)

As a supplement to the microscopic study of transformation behaviour in the uranium - 2 w/o - zirconium alloy the transformations in uranium and uranium-zirconium alloys containing 0.5, 2 and 5 w/o zirconium were investigated by means of DTA using argon as protective atmosphere. The results of these measurements are summarized in figs. 21 and 22. The curves represent the temperature difference between the specimen studied and a reference sample of platinum (which has no
allotropic transformations) during heating (fig. 2l) and cooling (fig. 22) at a rate of 10 °C per minute. In general the temperature difference is zero but when a transformation occurs on heating the uranium or uranium - zirconium alloy, its temperature will decrease due to heat absorption. This is reflected as a dip in the DTA-curve. Similarly the heat evolved during transformation on cooling will cause a peak in the curve. On heating the start of transformation corresponds to the point of deflection on the low temperature side of the dip and the end of transformation to the minimum point. The opposite conditions prevail for cooling.

The DTA-curves recorded always exhibited a slight change in temperature difference between the two samples, noticeable as a moderate and slowly varying slope. This effect was probably caused by oxidation of the uranium or uranium - zirconium alloy due to oxygen impurities in the argon gas and to differences in heat transfer properties for the two samples. The presented curves have been corrected for this background drift and show only the very distinct dips and peaks in the recorded curves.

The transformation temperatures in uranium and uranium - zirconium alloys are subject to considerable hysteresis. Thus, it has been shown by Duwez (17) that the transformation temperatures in uranium can be suppressed by more than 100 °C on rapid cooling. Therefore it would be desirable to carry out the DTA-measurements at a slow rate of temperature change but a limit is set for this rate in that too slow a temperature change will result in poor resolution of dips and peaks. The selected rate of 10 °C per minute appears to be convenient for the type of experiments reported here.

The temperature scale in the recorded DTA-curves is to be considered as a relative scale only since its measurement is carried out under a non-steady state. The recorded temperature may therefore not be representative for the exact temperatures of the two samples. There might also between runs be slight changes in the environment of the hot
junctions of the thermocouples leading to different recorded temperature scales in separate runs. To overcome these difficulties a common temperature scale was established by carrying out DTA-measurements for the uranium-zirconium alloys also against pure uranium. The start of the transition from α to β on heating was set at 666 °C in the pure uranium in accordance with the results of Klepfer and Chiotti (18). It is reasonable to adopt this value for the present experiments since the suppression of the transformation on cooling at 10 °C per minute amounts to a few degrees only according to Duvez and the overshoot on heating at this rate is likely to be less. With this temperature scale the transformation temperatures as obtained for pure uranium with DTA are in good agreement with the values obtained by resistance measurements by Klepfer and Chiotti as shown in the following table.

Check of the established temperature scale for DTA-measurements.

<table>
<thead>
<tr>
<th></th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β_s</td>
<td>β_f</td>
</tr>
<tr>
<td>Klepfer and Chiotti (18)</td>
<td>666</td>
<td>690</td>
</tr>
<tr>
<td>DTA, this investigation</td>
<td>666</td>
<td>690</td>
</tr>
</tbody>
</table>

The subscripts s and f refer to start and finish.

The accurate positioning of the dips and peaks for the uranium-zirconium alloys in the DTA curves was greatly facilitated by measurements against the uranium sample.

It is seen in fig. 21 that the temperature for the start of β-formation on heating is raised at least 5 °C by the addition of 0.5 w/o zirconium. A further rise is evident at increased zirconium content. Possibly the zirconium content has a delaying effect on the nucleation of β on heating. The transition of β to γ is lowered at 0.5 w/o zirconium in accordance with the phase diagram, fig. 1. Following this diagram in the interpretation
of the heating curve for the 2 w/o zirconium alloy it is seen that the
transition from $\alpha (+\gamma_2)$ to $\beta (+\gamma_2)$ is soon followed by the reaction
$\beta + \gamma_2 \rightarrow \beta + \gamma_1$. The corresponding dips overlap. The continued trans-
formation of $\beta + \gamma_1$ to $\gamma$ occurs over a temperature interval which is
reflected in the flattening of the curve on the high temperature side of
the minimum. In the heating curve for the 5 w/o zirconium alloy the
reactions $\alpha (+\gamma_2) \rightarrow \beta (+\gamma_2)$ and $\beta + \gamma_2 \rightarrow \beta + \gamma_1$ overlap completely.
The last reaction could also be considered as $\beta + \gamma_2 \rightarrow \gamma_1$ since 5 w/o
zirconium is very close to the eutectoid composition for this reaction.
If there is a temperature interval over which the transition occurs due
to non-eutectoid composition it is too small to be reflected in the DTA-
curve. The dips observed at about 625 °C in the 2 and 5 w/o zirconium
curves correspond to the $\delta \rightarrow \gamma_2$ transition.

On cooling (fig. 22) the corresponding transformations are ob-
served although displaced to lower temperatures because of the hysteresis
effect. In the 2 w/o zirconium alloy the $\gamma$ to $\beta$ transition is suppressed
so much that most of it occurs in the ($\beta + \gamma_2$)-region of the phase diagram.
Consequently no transformation over a temperature interval is reflected
by the curve. For the 5 w/o zirconium alloy the peaks corresponding to
$\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ reaction overlap as was also the case on heating.

The transition temperatures found in the uranium - zirconium alloys
agree qualitatively with the phase diagram of Howlett and Knapton (1),
fig. 1. The hysteresis effects, however make a quantitative comparison
difficult. Particularly large hysteresis is encountered for the $\alpha + \gamma_2 \rightarrow \beta + \gamma_2$
reaction.

The integrated area over a dip or under a peak is a measure of the
heat of reaction. In pure uranium the values of $\Delta H$ are 714 and 1166
cal/mole for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ reactions respectively (19). The corre-
sponding areas from the DTA-curves roughly agree with these figures.
It is also noticeable that the area for the $\delta \rightarrow \gamma_2$ reaction increases as the
amounts of these phases increase at increasing zirconium content. How-
ever, the ordinate scales for the separate runs may be slightly different
and only qualitative comparisons should be made.
4. Discussion

The phase diagram

The present results are in good agreement with the phase diagram according to Howlett and Knapton. The slight discrepancies as regards transformation temperatures are not surprising considering the hysteresis effects encountered in the phase changes.

There is a possibility that the eutectoid reaction $\beta \rightarrow \alpha + \gamma_2$ at 662 °C as proposed by Howlett and Knapton should be replaced by a peritectoid reaction $\beta + \gamma_2 \rightarrow \alpha$ at a slightly higher temperature since the DTA heating curves indicate a rise in transition temperature when zirconium is added to uranium. As pointed out, however, this effect could also be due to the delayed nucleation of $\beta$ caused by the presence of zirconium.

The DTA-curves for the 2 and 5 w/o zirconium alloys clearly demonstrate the transition $\gamma_2 \rightarrow \delta$ at about 610 °C which is a further confirmation of the stability of the $\delta$-phase. In constructing the TTT-diagram (fig. 17) the bend at 610 °C in the curve for the end of $\gamma$ transformation has been associated with this transformation. However, an alternative explanation as to the occurrence of the bend will be given below.

Mechanisms of transformation

Transformations in uranium alloys are frequently of the martensite type. The direct transformation of $\gamma$ to $\alpha$ found in the present experiments could definitely be termed martensitic since it has been possible to define a $M_t$ temperature for the reaction and since the amount of $\alpha$ formed increases at lower temperatures. According to Klepfer and Chiotti (18) all transformations in pure uranium exhibit martensitic features. These authors were able to show that the amount of transformed phase close to the equilibrium temperature is a function of temperature and that the transformations proceed rapidly under burst phenomena. They concluded that at least the nucleation should involve the formation of coherent nuclei. This type of nucleation is believed to be characteristic also for the Widmanstätten plates observed in the present investigation. The growth of
of such plates may occur by an atom by atom diffusion process or by a shear mechanism in which case the reaction is to be considered as martensitic. The probable mechanisms encountered during isothermal transformation of \( \gamma \) will be discussed in terms of these concepts.

In the \((\beta + \gamma_1)\)-region the precipitation of \( \beta \) is likely to be controlled by zirconium diffusion. The nuclei are believed to be coherent to a large extent, also for the \( \beta \)-particles nucleated at grain boundaries. This is inferred from the observation that on slow cooling, Widmanstätten plates start to grow from and are continuous with the rounded \( \beta \)-islands (figs. 18 and 19) which presupposes a definite orientation relation between the lattices of the \( \beta \)- and \( \gamma \)-phases already from the start of \( \beta \)-formation.

Slightly below the eutectoid temperature at 700°C, \( \beta \) and \( \gamma_2 \) form simultaneously, the \( \beta \)-phase exhibiting marked Widmanstätten character. Adopting the terminology suggested by Hillert (20) the process may be described as cooperative growth implying that the two phases grow together as an aggregate, thereby accelerating each other’s growth rates. As pointed out by Hillert both pearlite and bainite in steel can be described on this basis and the difference in their modes of formation is not clear. The evidence of analogous types of aggregates in the present case (fig. 7) is to be noted. It is possible that their mechanisms of formation are basically the same, e.g., the morphology might be determined by the Widmanstätten orientation of \( \beta \) in both instances.

At somewhat lower temperatures \( \beta \) as Widmanstätten plates is the only phase formed at the initial period of transformation (fig. 8). Since the subsequent precipitation of \( \gamma_2 \) occurs within the \( \beta \)-plates these are initially assumed to be supersaturated on zirconium by inheriting the zirconium content of the matrix. The growth process should then not require long range zirconium diffusion, as postulated for \( \beta \)-growth above the eutectoid temperature, although it might still occur in mean of diffusion jumps across the advancing interface. (On furnace cooling through this temperature region long range diffusion of zirconium seems to be of importance since it is observed that the last \( \gamma \) transforms at about 670°C which probably implies zirconium enrichment in that \( \gamma \)).
In the \((a + \gamma_2)\)-region supersaturated Widmanstätten plates of \(a\) are believed to form directly from \(\gamma\) in a manner similar to that described for \(\beta\) in the \((\beta + \gamma_2)\)-region. However, the bend at 610 °C in the curve for completed \(\gamma\)-transformation might possibly indicate a transition in the growth mechanism from a diffusion to a shear process since the reaction rate is markedly increased below this temperature. Such a transition provides a more likely explanation for the bend than does the phase change \(\gamma_2 \rightarrow \delta\) since the growth mechanism should be unaffected by a subsequent precipitation process within the transformed phase. White (21) observed a similar discontinuity in the transformation of low chromium uranium-chromium alloys and he attributed this to a change from diffusion to martensitic growth. Below about 610 °C the transformation of \(\gamma\) should then occur by the martensitic formation of supersaturated \(a\). However, at temperatures below about 490 °C this reaction is preceded by the partial transformation of \(\gamma\) to large \(a^1\)-plates, i.e., the transformation proceeds by two successive and possibly competitive martensite reactions. The crystallographic features of these reactions might differ but the transformation products are probably the same, apart from their morphologies.

**Precipitation within the transformation products**

The supersaturated Widmanstätten plates of \(\beta\) and \(a\) formed on isothermal transformation, rapidly reject their excess of zirconium by the precipitation of \(\gamma_2\) above 610 °C and of \(\delta\) below this temperature. It seems as if the initial precipitation is somewhat slower at 690 than 650 °C. This is obvious both from the metallographic observations and from the decrease in initial hardness (fig. 14). However, the overall process requires longer times the lower the temperature. It has not been possible to outline the start and end of these reactions in the TTT-diagram. They seem to start in the individual Widmanstätten plates shortly after their formations (cf selftempering of martensite in steel). The experimental methods used are not capable of determining the end of the precipitation reactions which also involve the coalescence and the decrease in number and increase in size of the precipitated particles.
Particles of γ₂ will transform to δ on quenching. This reaction probably occurs in situ as has been shown by Holden and Seymour (22) for massive δ-phase alloy.

The β to α transformation

It is a striking fact that the appearance after etching of the Widmanstätten plates does not change markedly when the transition temperature at 660 °C is passed. Possibly this has been one of the reasons for the outlining of the phase diagram as proposed by Saller et al (5). The transformation of β-plates to α on quenching probably occurs in situ as demonstrated by figs. 9 a and b. This is also true for the β formed above the eutectoid temperature at 700 °C (figs. 5 a and b). To a large extent the β-units seem to be transferred to single crystals of α which, however often display subgrains. The subgrains are believed to result from strain-induced polygonization caused by the volume changes accompanying the transformation as has been shown by Chiswik and Lloyd (23) and Cahn and Tomlinson (24). The character of an in situ transformation is probably preserved as long as differences in the dissolved zirconium content and in states of stress exist between adjacent β-crystals. When precipitation reactions have come to an end, however, the boundaries become more mobile leading to the observed crystal growth or recrystallization.

5. Summary and conclusions

Phase transformations in a uranium-zirconium alloy containing 2 weight percent zirconium have been studied with the microscope after heat treatments comprising isothermal transformation of γ in the temperature region 720 to 100 °C and cooling from the γ-range at various rates. The transformations on heating and cooling of a series of uranium-zirconium alloys containing 0, 5, 2 and 5 w/o zirconium have been studied by means of differential thermal analysis and the results have been correlated with the transformations in technically pure uranium. The findings are compatible with the uranium-zirconium phase diagram proposed by Howlett and Knapton (1) but not with the diagram according to Saller, Rough and Bauer (5).
The isothermal transformation study has been summarized in a time-temperature-transformation diagram. The various reactions occurring during isothermal transformations and their corresponding mechanisms have been suggested as follows.

a) **Above 700 °C.** \(\beta\)-phase is precipitated mainly as Widmanstätten plates. The growth is controlled by zirconium diffusion. The equilibrium structure consists of \(\beta + \gamma\).

b) **At and slightly below 700 °C.** \(\gamma\) transforms by the diffusion controlled cooperative growth of \(\beta\) and \(\gamma_2\).

c) **Between 690 and 660 °C.** \(\gamma\) transforms to supersaturated Widmanstätten plates of \(\beta\) which subsequently precipitate particles of \(\gamma_2\). The growth is probably diffusion controlled.

d) **Between 660 and 610 °C.** \(\gamma\) transforms to supersaturated Widmanstätten plates of \(\alpha\) which subsequently precipitate particles of \(\gamma_2\). The growth is probably diffusion controlled.

e) **Between 610 and 490 °C.** \(\gamma\) transforms to supersaturated \(\alpha\) in the shape of plates and needles and possibly by a martensitic reaction. From the \(\alpha\)-phase, particles of \(\delta\) are subsequently precipitated.

f) **Between 490 °C and room temperature.** \(\gamma\) transforms to supersaturated \(\alpha\) by two successive and possibly competitive martensitic reactions. In the first reaction part of the \(\gamma\) transforms to fairly large lens shaped plates called \(\alpha^1\) and in the second, the remaining \(\gamma\) transforms to a fine acicular structure analogous to that described under e). The number of \(\alpha^1\)-plates increases at lower temperatures. From both structure types \(\delta\) particles are subsequently precipitated but this reaction is extremly sluggish.

The \(\beta\)-phase is not retained but transforms to \(\alpha\) upon quenching. This transformation often seems to involve the formation of single
α-crystals from each individual Widmanstätten plate of β. These α-crystals often contain subgrains, probably as a result of strain-induced polygonization. Widmanstätten plates of supersaturated β or α disappear, subsequent to the precipitation of secondary phases, as a result of grain growth or recrystallization.

Cooling from the γ-range at various rates yields structures that are easily interpreted from the time-temperature-transformation diagram. It is established that the addition of 2 weight percent zirconium to uranium markedly refines the grain size.

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Fig. 1
Uranium-zirconium phase diagram according to Howlett and Knapton (1).
Fig. 2
Uranium-zirconium phase diagram according to Saller, Rough and Bauer (5).
Fig. 3 900°C 15 min., quenched. Plates of α'.

a) Citric acid etch.  x 500.

b) Same area unetched, polarized light.  x 500.

Fig. 4 900°C 15 min., quenched to 720°C, isothermally transformed 15 min., quenched. Bright phase at γ-grain boundaries.  x 500.

Fig. 5 900°C 15 min., quenched to 720°C, isothermally transformed 30 min. Bright phase as Widmanstätten plates and grain boundary rim.

a) Citric acid etch.  x 500.

b) Same area unetched, polarized light.  x 500.
Fig. 6  900°C 15 min., quenched to 720°C, isothermally transformed 1 h. Bright phase partly spherodized. x 500.

Fig. 7  900°C 15 min., quenched to 700°C, isothermally transformed 2 min. Bright phase containing ridges of secondary precipitate. x 2000.

Fig. 8  900°C 15 min., quenched to 690°C, isothermally transformed 30 sec. Widmanstätten plates with wrinkled surfaces in α'-matrix. x 750.
Fig. 9 900°C 15 min., quenched to 690°C, isothermally transformed 2 min. Widmanstätten plates with ridges.

a) Citric acid etch. x 750.

b) Same area unetched, polarized light. x 750.

Fig. 10 900°C 15 min., quenched to 690°C, isothermally transformed 30 min.

a) Citric acid etch. Secondary precipitate in smooth matrix. x 750.

b) Same area unetched, polarized light. Grain structure of matrix. x 750.
Fig. 11 900°C 15 min., quenched to 690°C, isothermally transformed 24 h. Secondary precipitate. x 750.

Fig. 12 900°C 15 min., quenched to 575°C, isothermally transformed 10 min. Mottled Widmanstätten plates.

a) Citric acid etch. x 1200.

b) Same area unetched, polarized light. Note uniform orientation of plates nucleated at the grain boundary. x 1200.
Fig. 13 900°C 15 min., quenched to 575°C, isothermally transformed 144 h. Secondary precipitate in smooth matrix. x 1200.

Fig. 15 900°C, quenched to 350°C, isothermally transformed 10 min. Large $\alpha'$-plates in finely acicular matrix. Note the previous $\gamma$-grain boundary. x 750.

Fig. 16 900°C 15 min., quenched to 100°C, isothermally transformed 10 min. Large and fine $\alpha'$-plates. x 750.
Vickers hardness (5 kg load) as function of time in isothermal transformation. Each reported value is an average of 10 measurements.
Fig. 17

Time-temperature-transformation diagram for a uranium-2 w/o-zirconium alloy.
Fig. 18 800°C 1 h, furnace cooled at 2°C per minute to 690°C, quenched. Outgrowth of Widmanstätten plates from rounded β-phase particle.  x 750.

Fig. 19 800°C 1 h, furnace cooled at 2°C per minute to 680°C, quenched. Widmanstätten fringes growing from rounded β-plates and isolated β-plates within the matrix.  x 250.

Fig. 20 800°C 1 h, furnace cooled at about 2°C per minute to room temperature. Ionic bombardment etch. Widmanstätten pattern outlined by secondary precipitate.  x 750.
Differential thermal analysis heating curves.

Fig. 21
Fig. 22
Differential thermal analysis cooling curves.