



Report No. BMI-1092  
Metallurgy and Ceramics  
(M-3679, 17th Ed.)

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**UNCLASSIFIED**

Contract No. W-7405-eng-92

THE STABILITY AND EXISTENCE RANGE  
OF THE ZIRCONIUM-URANIUM EPSILON PHASE

by

Frank A. Rough  
Alfred E. Austin  
Arthur A. Bauer  
J. Robert Doig

Classification cancelled (or changed to UNCLASSIFIED)  
by authority of Dr. from Declassification Branch  
dated July 5, 1956, date 9-6-56  
by Paul H. Yers TIE

May 28, 1956



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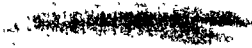
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THE STABILITY AND EXISTENCE RANGE OF THE  
ZIRCONIUM-URANIUM EPSILON PHASE

Frank A. Rough, Alfred E. Austin,  
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*Data which show the intermediate zirconium-uranium epsilon phase to be a thermodynamically stable phase are presented and the zirconium-uranium constitutional diagram is shown.*

*The effect of oxygen and nitrogen on zirconium-uranium alloys, and on epsilon-phase alloys in particular, is shown. Ternary zirconium-uranium-oxygen diagrams are presented.*

*A two-phase beta zirconium-plus-epsilon region extends from about 44 to 57 or 58 w/o uranium. The solubility limits of the epsilon region narrow with decreasing temperature. At 550 C these limits are estimated to be about 45 and 53 w/o uranium.*

*Isotherm temperatures on either side of the epsilon phase show a difference of 14 C. Thermal-analysis data, which are believed the most reliable data obtained in indicating absolute temperatures, show these temperatures to be 593 and 607 C on the zirconium- and uranium-rich sides of the epsilon phase, respectively.*

*Less than 500 ppm oxygen is soluble in the epsilon phase. Maximum solubility occurs at some composition between 50 and 55 w/o uranium.*

*A change in rate of thermal expansion of the epsilon phase at low temperatures suggests the possibility of some structural change. The nature of this change is unknown.*

INTRODUCTION

Zirconium-uranium alloys have long been considered for use as reactor fuels because of the low thermal-neutron cross section of zirconium. Of particular interest recently has been the zirconium-50 w/o uranium alloy, in which there has been evidence of an intermediate phase.

However, this alloy was regarded with uncertainty because its stability was questionable, the intermediate epsilon phase having been reported<sup>(1)</sup> as a transition phase in the decomposition of beta zirconium to

(1) References at end of report.

the terminal alpha-uranium and alpha-zirconium phases. Recent investigations of the phase relationships between zirconium and uranium dioxide<sup>(2)</sup> have indicated that this decomposition, rather than being an indication of epsilon instability, occurs as a result of oxygen contamination, oxygen stabilizing the two alpha phases with respect to the epsilon phase.

In order to clear up the reported discrepancies in zirconium-uranium alloy constitution and behavior, an investigation was undertaken for WAPD to determine if the epsilon phase is indeed stable, and if it is, to determine its existence range with respect to temperature and composition.

### EXPERIMENTAL PROCEDURES

For this investigation, alloys ranging in composition from 40 to 60 w/o uranium were prepared. These included a number of alloys with varying oxygen contents and a few alloys with varying nitrogen contents.

Specimens were prepared and examined using various methods. Specimens, heat treated under various conditions, were examined metallographically and by X-ray techniques. Thermal-analysis data were obtained and a number of alloys were examined with a high-temperature X-ray camera.

#### Alloy Preparation

In order to investigate the thermodynamic stability of the epsilon phase, a powder compact of approximately zirconium-50 w/o uranium composition was prepared by degassing a compact consisting of uranium and zirconium hydride powders. The uranium powder was prepared by hydriding and dehydriding biscuit uranium; the zirconium hydride was prepared from crystal bar zirconium. Zirconium hydride rather than zirconium powder was used as the starting material in an attempt to minimize contamination during handling.

The powders were mixed, compacted, and transferred to a vacuum furnace under an argon atmosphere. The compact was then heated to the desired annealing temperature of 538 C over a 3-day period. The temperature was increased in 28 or 55 C intervals from 150 to 538 C to permit gradual degassing, the pressure never being permitted to exceed  $50 \times 10^{-3}$  mm of mercury. There was no evidence of hydrogen evolution on heating above 425 C, indicating that the dehydriding process was essentially complete below this temperature.



Alloys containing 40, 45, 50, 55, and 60 w/o uranium were prepared from biscuit uranium and zirconium of three different oxygen levels: crystal bar zirconium containing about 50 ppm oxygen; normal sponge zirconium containing about 1000 ppm oxygen; and sponge zirconium to which oxygen was added to bring its oxygen level to about 3000 ppm. The alloys were double melted by consumable-electrode arc-melting techniques. The final ingots were forged and rolled at temperatures between 790 and 840 C to the shapes desired.

Additional alloys containing 46, 48, 52, and 54 w/o uranium were prepared from crystal bar zirconium by a tungsten-electrode arc-melting technique. These were cast into wire-bar form, sealed under argon in cold-rolled steel tubes, and rolled at 815 C to 1/4-in. rod.

Two series of zirconium-49 w/o (27 a/o) uranium alloys containing up to 20 a/o oxygen or up to 18 a/o nitrogen were prepared by arc melting biscuit uranium and crystal bar zirconium with either fused  $\text{UO}_2$  or compacted UN powder. The actual nitrogen compositions are believed to be lower than those intended, due to loss of UN by spattering during melting. This spattering was not observed with the fused  $\text{UO}_2$ .

Nominal compositions, which are referred to throughout this report, are listed in Table 1 along with compositions determined by analysis.

### Heat Treatment

The dehydrated zirconium-uranium powder compact was annealed in a vacuum furnace at 538 C for 14 days and furnace cooled. The pressure was maintained at  $10^{-5}$  mm mercury during this period.

The two series of arc-melted alloys of base zirconium-49 w/o (27 a/o) uranium composition with additions of up to 20 a/o oxygen and 18 a/o nitrogen, respectively, were homogenized 20 hr at 1095 C. Samples were subsequently annealed for 100 hr at 550 and 660 C, respectively, and water quenched. The samples were annealed in a vacuum furnace under a pressure of  $10^{-4}$  mm mercury.

Specimens containing 45, 46, 48, 50, 52, 54, and 55 w/o uranium, prepared from crystal bar zirconium, were annealed for 4 and 8 weeks at 550 C, and for 10 weeks at 300 and 400 C.

In addition, a series of specimens containing 45, 50, 55, and 60 w/o uranium, prepared with zirconium with oxygen levels of about 50, 1000, and 3000 ppm, was annealed 1 hr at 800 C, water quenched, and reannealed 3 weeks at 550 C and water quenched. All of these specimens were laid on

TABLE 1. ZIRCONIUM-URANIUM ALLOY COMPOSITION

Nominal Composition, w/o				Analyzed Composition, w/o			
Zr	U	N	O	Zr	U	N	O
60	40	-	0.003	-	40.5	0.004	-
55	45	-	0.00275	-	46.0	0.003	-
55	45	-	0.055	-	-	-	-
55	45	-	0.165	-	-	-	-
50	50	-	0.0025	-	49.9	0.005	-
50	50	-	0.050	-	50.2	0.005	0.061
50	50	-	0.150	-	-	-	0.1780
45	55	-	0.00225	-	55.8	0.003	-
45	55	-	0.045	-	-	-	-
45	55	-	0.135	-	-	-	-
40	60	-	0.002	-	61.2	0.005	-
40	60	-	0.040	-	59.8	0.007	0.069
40	60	-	0.120	-	-	-	-
54	46	-	0.0027	-	-	-	-
52	48	-	0.0026	-	47.6	-	-
48	52	-	0.0024	-	51.5	-	-
46	54	-	0.0023	-	53.9	-	-

Nominal Composition, a/o			
Zr	U	N	O
73	27	-	-
72	26	-	2
70.5	24.5	-	5
68	22	-	10
65.5	19.5	-	15
63	17	-	20
72	26	2	-
71.5	25.5	3	-
70.5	24.5	5	-
69	23	8	-
67	21	12	-
64	18	18	-

tantalum foil and sealed in evacuated Vycor tubes. Zirconium chips placed in a bulb at one end of the tube were heated to getter the residual gases in the tube, the bulb being sealed off prior to heat treatment.

### Thermal-Gradient Technique

In order to investigate the existence range of the beta zirconium-plus-epsilon region, specimens were annealed in a furnace producing a gradient in temperature of about 550 to 650 C over a 5-in. length. The specimens were subsequently examined to determine the presence of a two-phase region appearing near the central portion of the specimen.

The 40, 45, 46, 48, 50, 52, 54, 55, and 60 w/o uranium alloys were studied by this method. Initially, rod samples, furnace cooled from 800 C, were alternately cold swaged and annealed at 550 C, finally being machined to 1/8-in. -diameter rod about 5 in. long. Additional specimens of the 45, 50, 55, and 60 w/o uranium alloys were later machined from rod quenched from 800 C.

Due to the furnace-tube size, it was possible to heat treat only two specimens at a time. These were first wrapped in tantalum foil and were then sealed in an evacuated Vycor tube which was gettered by zirconium chips. Thermocouples were fastened to the Vycor tube at 1-in. intervals along its length and comparative measurements were made of their position with respect to the specimens. Temperature was recorded on a six-point recorder. The assembly was then inserted in a wire-wound furnace in which the spacings were adjusted to produce a gradient in temperature of about 100 C over a 5-in. length. The specimens were held at temperature for 1 week and were water quenched.

An attempt was made to determine if the temperatures, as indicated by the thermocouples placed on the outside of the Vycor tube in which the specimens were contained, were the true specimen temperatures. A Vycor tube was prepared with thermocouple leads extending into the tube, the thermocouple being spot welded to a dummy specimen. Readings taken on this thermocouple were compared with readings taken on a thermocouple placed outside the tube at the same depth in the furnace. The thermocouple readings were found to show reasonable agreement, the inner thermocouple attached to the dummy specimen reading a maximum of 2 C below the outer thermocouple.

This comparison does not, however, take into account the tantalum foil in which the specimens were wrapped. It may be expected that the foil will act as a radiation shield, thereby further reducing the actual specimen

temperature below that shown by the indicating thermocouple. Upon this basis it is felt that the specimen temperatures are more than 2 C below the measured values, although the exact differences between the two are unknown.

### Metallography

All specimens for metallographic examination were mounted in Bakelite or Castolite and were wet ground through 600-grit paper. In order to develop satisfactorily etched structures, several polishing and etching techniques were investigated. The most consistently successful procedure was to polish on Forstmann's cloth using stannic oxide abrasive and to follow this with an etch-polish on billiard cloth using Linde B abrasive and a solution consisting of 200 cm<sup>3</sup> water, 10 cm<sup>3</sup> nitric acid, and 1 g of ammonium bifluoride.


The specimens were etched with mixtures of lactic, nitric, and hydrofluoric acids in the ratios 30 cm<sup>3</sup>:30 cm<sup>3</sup>: 10 drops or 50 cm<sup>3</sup>:50 cm<sup>3</sup>: 5 drops.

The intermediate etch polish was omitted with some specimens and satisfactory structures were obtained. However, this step was retained for the majority of the specimens.

### X-Ray Diffraction Techniques

Three different types of specimens were examined by three different types of X-ray diffraction techniques: bulk alloy specimens were examined on metallographically polished surfaces on an X-ray diffractometer; slivers, cut from these specimens, were examined in a Debye powder camera; machined 0.080-in. -diameter rods were examined in a high-temperature X-ray camera. The bulk metallographic specimens were examined on a General Electric diffractometer with CuK alpha radiation. Slivers from these specimens, for use in a 57.3-mm powder camera, were made by grinding and then etching in a solution of nitric and hydrofluoric acids. Specimens for study at elevated temperatures were made by machining a 1/4-in. rod to 0.080 in. in diameter, the final rod being etched in a nitric-hydrofluoric acid solution.

The specimens examined in the high-temperature X-ray camera were annealed 1 hr at 800 C, furnace cooled to 500 C, held 5 hr and furnace cooled prior to machining. After machining and etching, the specimens were placed in the camera, which was then evacuated. Heating was



sufficiently slow to keep the pressure below  $4 \times 10^{-5}$  mm mercury during the initial outgassing period. At temperatures of 500 C and above, the pressure was kept below  $2 \times 10^{-6}$  mm mercury.

The specimen temperature was measured by means of a platinum-platinum rhodium thermocouple which was adjacent to the specimen. Temperature was calibrated by comparing the lattice expansion of a tantalum specimen with dilatometric thermal-expansion data. (3) Temperature stability was  $\pm 1$  C for 2 to 3-hr X-ray exposures. The specimens were held at temperature 1/2 hr before an X-ray exposure was begun.

### Thermal Analysis

In order to establish the temperature differences between the isotherms on either side of the epsilon phase, a comparative differential-thermal-analysis technique was employed to compare the transformation temperatures in zirconium-40, 50, 55, and 60 w/o uranium alloys.

Specimens for analysis consisted of two halves of 1/2-in. -diameter rods of different compositions, joined together to re-form a 1/2-in. -diameter specimen. Each half was 3/4 in. long. The temperature-measuring thermocouple was inserted in a hole drilled between the two specimens, while the differential thermocouples were inserted in holes drilled into each of the halves.

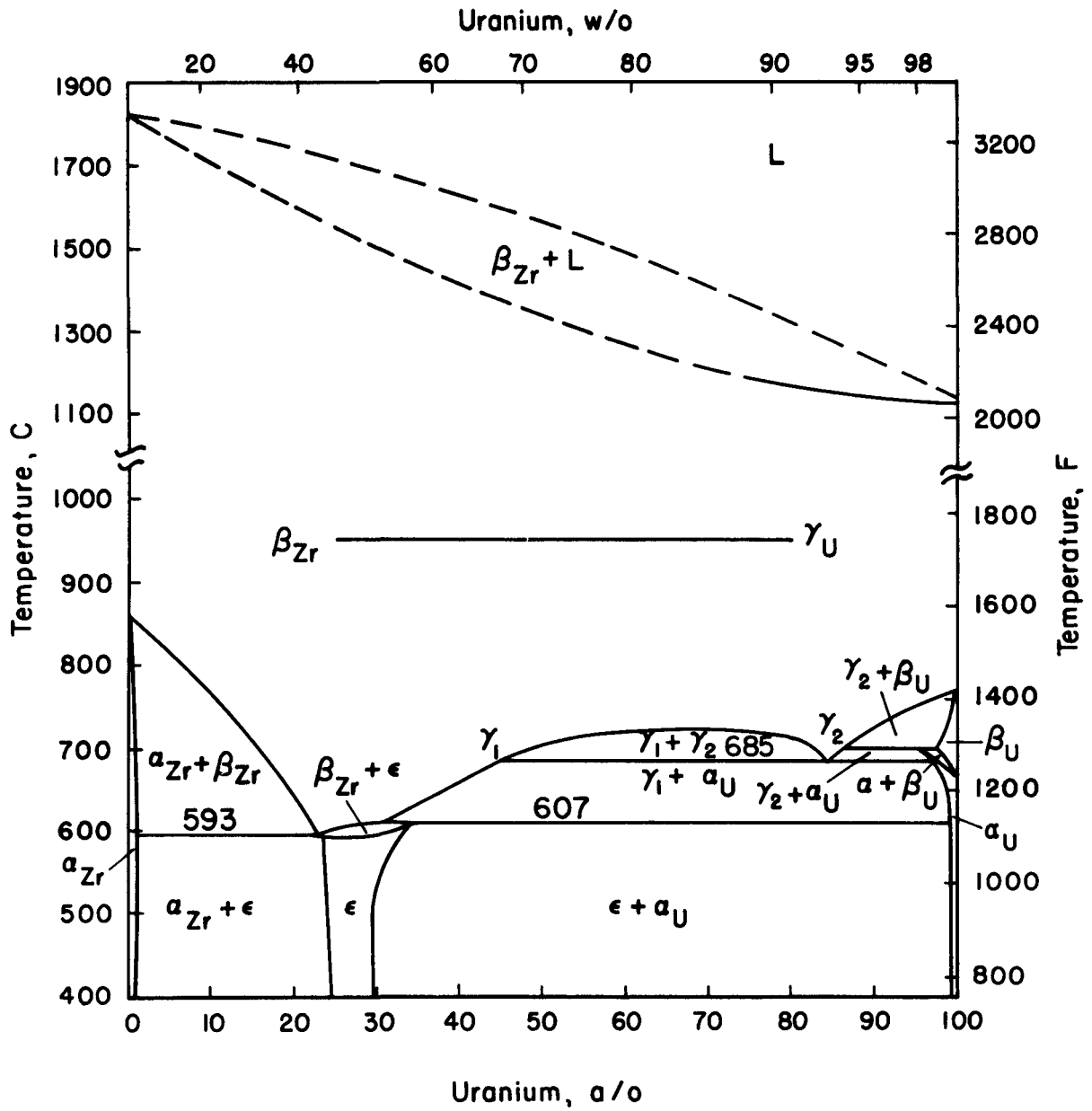
Specimens consisting of 40 and 50, 40 and 60, 50 and 60, 50 and 55, and 55 and 60 w/o uranium samples were prepared. They were heated at a rate of 1-1/2 C per min and data were obtained on an X-Y recorder.

## EXPERIMENTAL RESULTS AND DISCUSSION

Upon the basis of data obtained in this investigation, the zirconium-uranium constitutional diagram has been constructed as shown in Figure 1.

Data are presented which:

- (1) Show the epsilon phase to be stable.
- (2) Illustrate the ternary-alloy behavior of epsilon-phase alloys, oxygen and nitrogen additions causing the epsilon phase to decompose.



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FIGURE 1. ZIRCONIUM-URANIUM CONSTITUTIONAL DIAGRAM

- (3) Indicate the existence range of the epsilon phase with respect to temperature and uranium, zirconium, and oxygen compositions.

Thermal changes noted during the high-temperature X-ray studies also are presented.

### Epsilon-Phase Stability

X-ray diffraction examination of the specimen of compacted zirconium and uranium powders following the 14-day anneal at 538 C revealed the presence of alpha zirconium, alpha uranium, and epsilon. Relative intensities of these phases were weak, medium, and strong, respectively. The alpha phases are present as the result of incomplete reaction. Also, the alpha-zirconium lattice was found to be expanded as a result of oxygen and nitrogen contamination, which precludes the possibility of obtaining epsilon alone.

The formation of the epsilon phase from the elements without first forming the high-temperature beta phase shows that epsilon is a thermodynamically stable phase, and is not a transition phase in the decomposition of beta to the terminal alpha-uranium and alpha-zirconium phases.

Further evidence for the stability of the epsilon phase is presented in later sections of this report.

Metallographic evidence for the stability of the epsilon phase is shown by the gradient specimens in which beta appears above and epsilon appears below about 600 C, while over a small temperature interval epsilon exists in equilibrium with the beta phase.

Verification for the existence of this two-phase region over a small temperature interval was obtained during high-temperature X-ray studies. On repeated cycling through this region, beta and epsilon were consistently found above and below it, respectively, which is further evidence for the stability of the epsilon phase.

Thermal data also testify to the reversibility of the beta-to-epsilon transformation, with zirconium-rich alloys transforming at a slightly lower temperature than uranium-rich alloys.

The structure of the epsilon phase has not been fully determined; however, from available data it appears to be either hexagonal or rhombohedral. During high-temperature X-ray studies, the X-ray diffraction pattern of the epsilon phase could be best indexed on either a primitive

rhombohedral cell or the corresponding hexagonal cell. Cell dimensions of the epsilon phase,  $a_0$  and  $c_0$ , were calculated for the 45, 50, and 55 w/o uranium alloys at 575 to 580 C. The calculations were made by the least squares method using back reflection lines (805), (903), and (815). The results are given in Table 2.

TABLE 2. VARIATION OF LATTICE CONSTANTS OF EPSILON WITH COMPOSITION AT 575 C

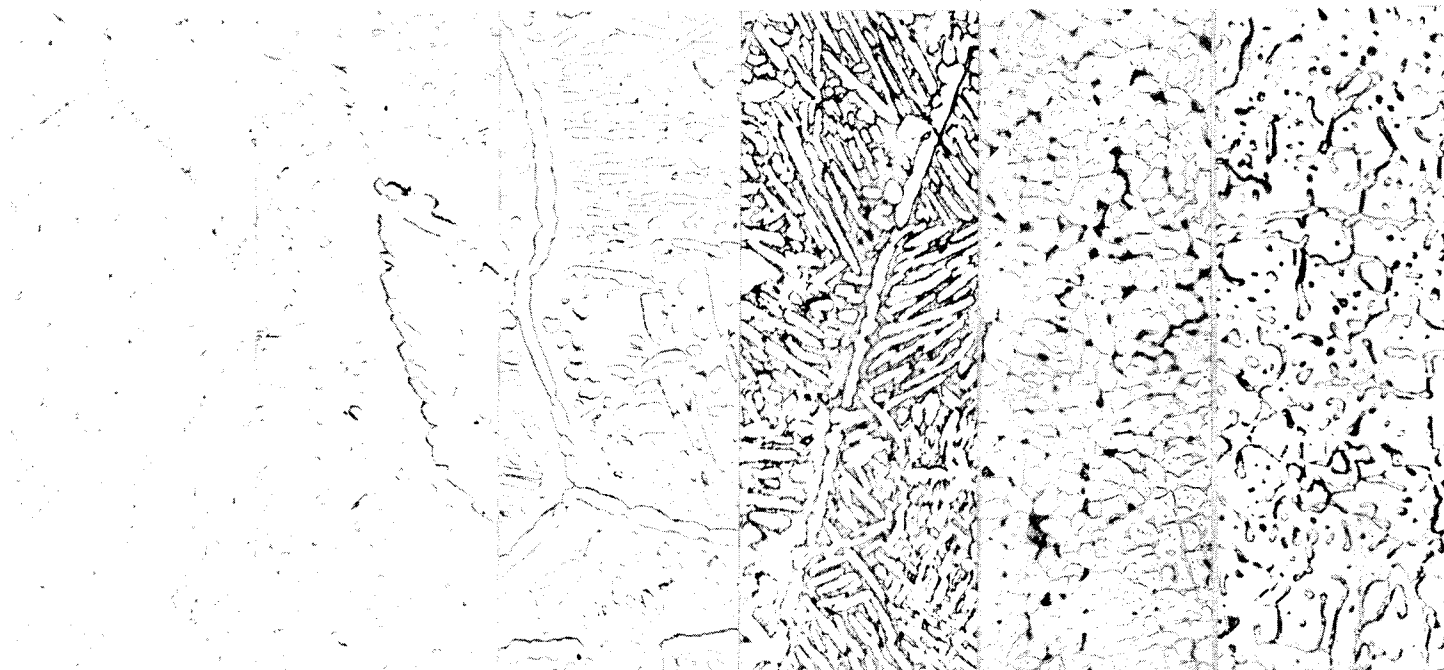
Uranium Content (Balance Zirconium), w/o	Lattice Constants	
	$a_0$	$c_0$
45	$8.790 \pm 0.002$	$9.233 \pm 0.010$
50	$8.793 \pm 0.002$	$9.212 \pm 0.007$
55	$8.779 \pm 0.0004$	$9.253 \pm 0.002$

The  $c_0$  dimension is expanded for both the 45 and 55 w/o uranium alloys compared with the  $c_0$  dimension of the 50 w/o uranium alloy. The  $a_0$  dimension is slightly contracted in the 55 w/o alloy. There is a net volume expansion for the 45 and 55 w/o uranium alloys compared with the 50 w/o alloy. This suggests that the ideal composition of the epsilon phase is close to the 50 w/o composition, with solid solution of zirconium and uranium, respectively, on either side of the 50 w/o composition.

Epsilon-Phase Decomposition Produced by  
Oxygen and Nitrogen

The observed decomposition of epsilon has been found to occur as a result of either oxygen or nitrogen contamination. The effect of oxygen on the epsilon phase is shown by the series of photomicrographs appearing in Figure 2. These photomicrographs were obtained from a series of base zirconium-27 a/o (49 w/o) uranium alloys with additions of up to 20 a/o oxygen. X-ray identification of the phases present and their relative intensities appear in Table 3. The phases identified are also shown below the photomicrographs.





	N29534	N29535	N29536	N29537	N29538	N29539
COMPOSITION: URANIUM, a/o	27	26	24.5	22	19.5	17
OXYGEN, a/o	-	2	5	10	15	20
PHASES IDENTIFIED:	$\epsilon + \alpha Z_r$	$\epsilon + \alpha Z_r$	$\epsilon + \alpha Z_r + \alpha U$	$\epsilon + \alpha Z_r + \alpha U$	$\alpha Z_r + \alpha U$	$\alpha Z_r + \alpha U$

**FIGURE 2. MICROSTRUCTURES OF ARC-MELTED ZIRCONIUM-27% a/o (49 w/o) URANIUM-BASE ALLOYS WITH INCREASING OXYGEN ADDITIONS**

HOMOGENIZED 1095 C; ANNEALED 100 HR AT 550 C AND WATER QUENCHED  
MAGNIFICATION: 250X

090  
090

TABLE 3. X-RAY IDENTIFICATION OF PHASES PRESENT IN BASE ZIRCONIUM-27 a/o (49 w/o) URANIUM ALLOYS WITH OXYGEN AND NITROGEN ADDITIONS

Additions to Base Alloy <sup>(a)</sup> , a/o	Intensity <sup>(b)</sup>		
	$\epsilon$	$\alpha$ Zr	$\alpha$ U
Alloy	S	0	0
2 oxygen	S	MF	0
5 oxygen	S	M	F
10 oxygen	S	S	MF
15 oxygen	0	S	MF to M
20 oxygen	0	MS	MF
2 nitrogen	S	MF	0
4 nitrogen	S	M	0
18 nitrogen	M	S	MF

(a) The base alloy is zirconium-27 a/o (49 w/o) uranium.

(b) Relative intensities of phases are designated as follows: S - strong, M - medium, MF - medium faint, F - faint.

Metallographic examination of specimens prepared from the same series of alloys but annealed at 660 C indicated essentially the same results with the exception that the epsilon phase was replaced by the high-temperature beta phase.

Upon the basis of these data and data obtained during the investigation of the phase relationships occurring between zirconium and uranium dioxide<sup>(2)</sup>, the ternary zirconium-uranium-oxygen diagrams for these temperatures are shown in Figures 3 and 4. The solubility of oxygen in the epsilon and beta phases is much lower than is shown in these diagrams, the diagrams being constructed primarily to provide a description of the phase relationships in this region.

It is clear from these diagrams that oxygen will cause the epsilon phase to decompose. With increasing amounts of oxygen, alpha zirconium and alpha uranium first appear in conjunction with epsilon; when sufficient oxygen is absorbed, the equilibrium phases are the two alpha phases only.

Data were obtained which show that nitrogen has the same restrictive effect on the epsilon phase. Zirconium-27 a/o (49 w/o) uranium alloys with nitrogen additions of between 0 and 18 a/o nitrogen were examined after having been annealed for 100 hr at 550 or 660 C. The microstructures of these alloys were similar to the ones shown for the oxygen-containing alloys in Figure 2. X-ray data obtained on specimens from the series annealed at 550 C are given in Table 3. However, the uranium and nitrogen contents of

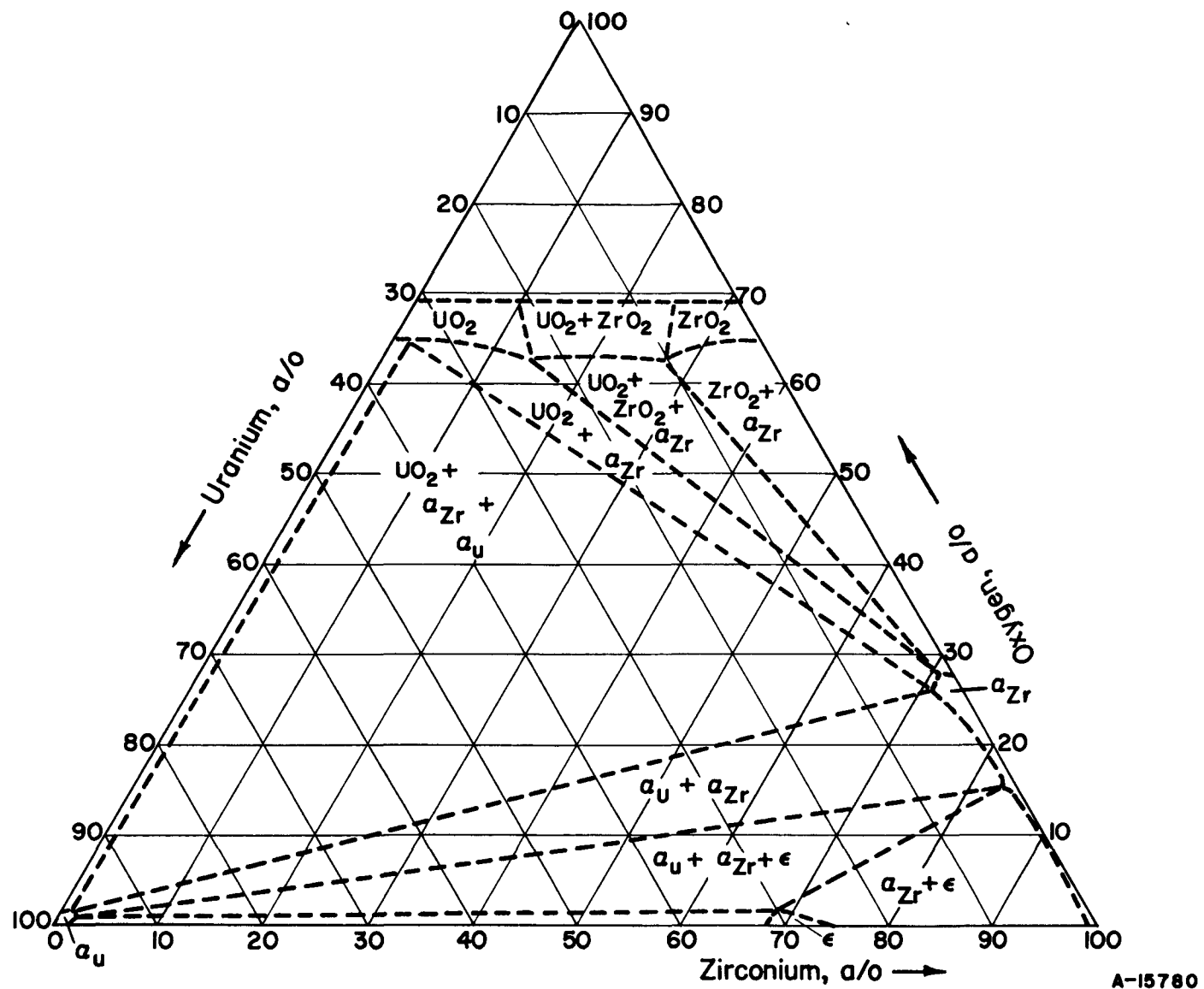


FIGURE 3. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 550 C

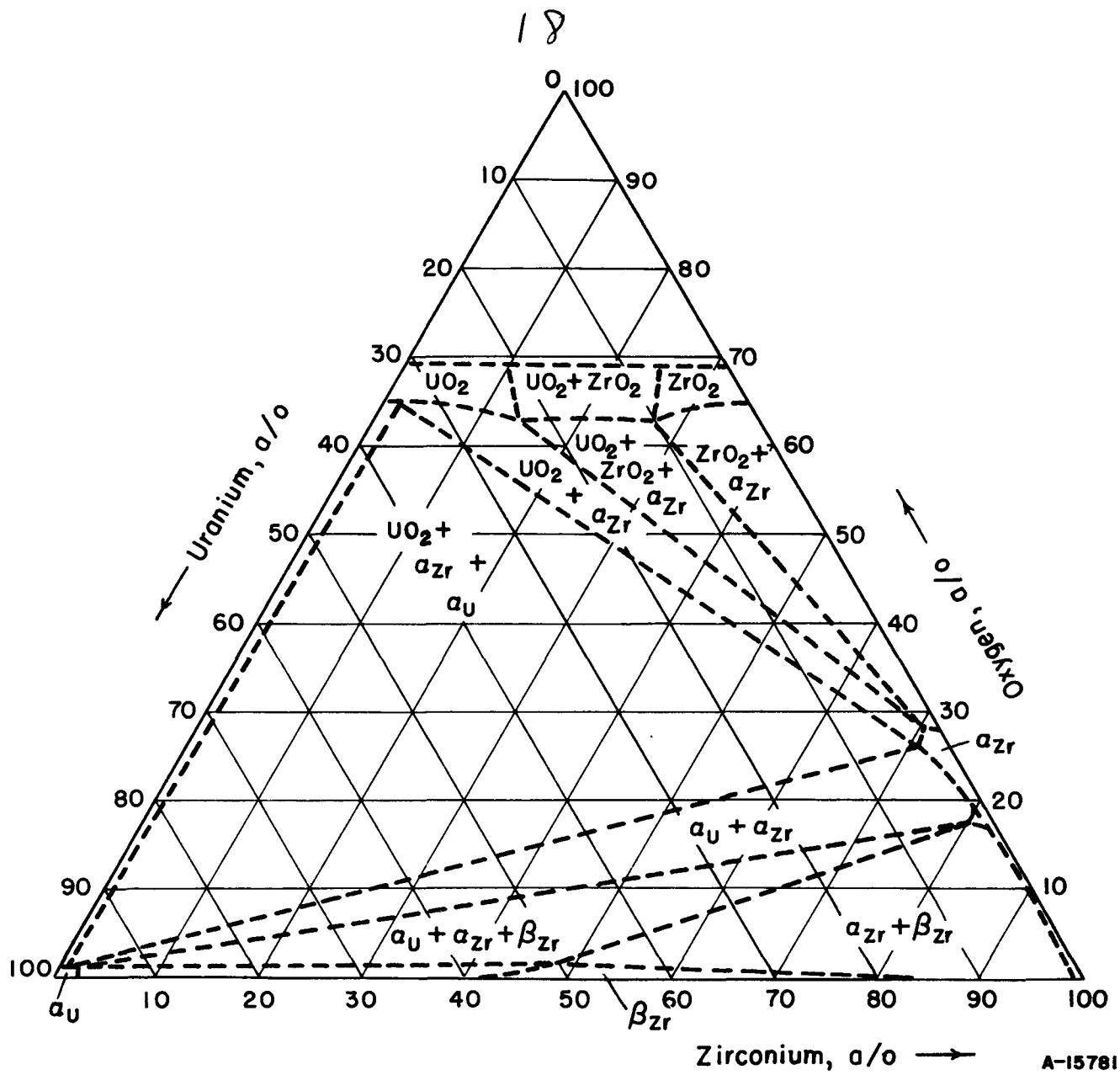


FIGURE 4. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 660 C

these alloys are believed to be high because of losses of uranium nitride powder experienced during melting. Consequently, these results are not viewed as being quantitatively accurate. However, they do show the same sequence of epsilon decomposition occurring with nitrogen additions as occurs with oxygen additions.

### Existence Range of the Epsilon Phase

Data indicating the existence range of the epsilon with respect to temperature and composition have been obtained.

#### Temperature of Isotherms

The temperatures of the isotherms were determined by a number of techniques and, while variations in the absolute temperature were obtained, the results were consistent in indicating that uranium-rich alloys transform at a temperature about 14°C higher than zirconium-rich alloys.

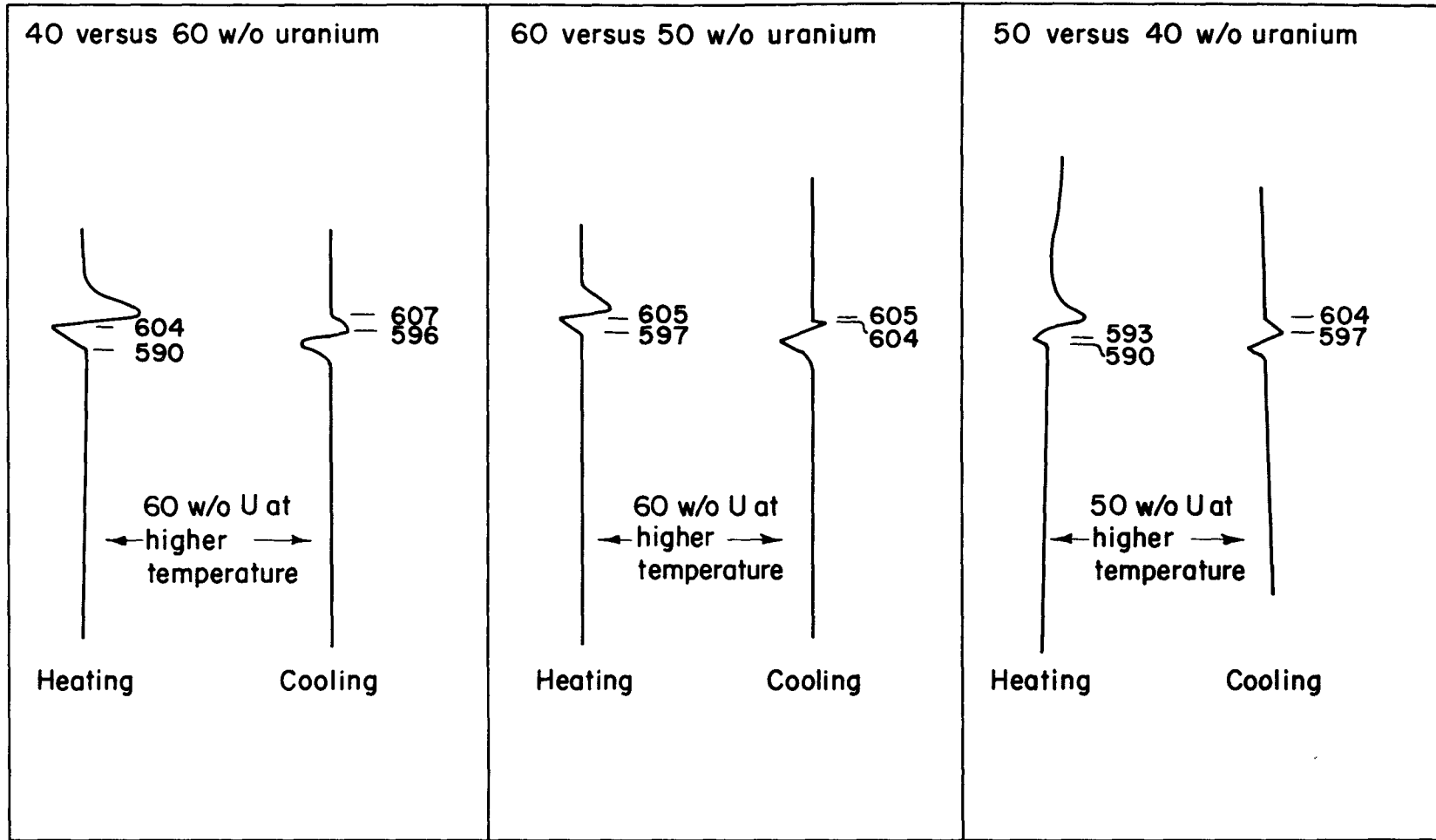
The absolute temperatures obtained by thermal analysis are regarded as more reliable than those obtained either from the temperature-gradient specimens or by high-temperature X-ray analysis. Temperature calibration is a likely source of error in these last two methods.

Thermal Analysis. Typical curves obtained by the comparative differential-thermal-analysis technique are shown in Figure 5. The beginning of transformation was indicated by a sharp deflection in the curves obtained on the majority of specimens analyzed. These deflections are produced by differences in temperature between the differential thermocouples.

The direction of deflection is significant, indicating which of the specimens is at a higher temperature and, therefore, denoting which specimen is undergoing transformation at a particular temperature. For instance, in the heating curve shown for the zirconium-40 and 60 w/o uranium samples, the 40 w/o alloy transforms initially as the 60 w/o alloy continues heating. A deflection to the left is therefore obtained indicating that the 60 w/o uranium sample is the hotter of the two samples. Finally, the 60 w/o alloy begins to transform and its temperature remains fairly constant. The transformed 40 w/o sample now becomes the hotter of the two samples, causing a deflection to the right. The directions in which the deflection occurs and their significance in terms of higher or lower sample temperatures had been predetermined in tests of the differential thermocouples.

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FIGURE 5. TYPICAL COMPARATIVE DIFFERENTIAL THERMAL-ANALYSIS CURVES FOR ZIRCONIUM-40, 50, AND 60 w/o URANIUM ALLOYS

It should be noted that only a small temperature difference exists between the zirconium-50 and 60 w/o uranium alloys for the start of transformation on cooling, whereas on heating the difference is sizable. The reverse effect is observed for the 40 and 50 w/o uranium specimens, a small temperature difference being observed on heating and a larger difference being observed on cooling. These relative differences are interpreted to mean that the 50 w/o uranium alloy transforms over a temperature range which is intermediate to the two isotherm temperatures shown for the 40 and 60 w/o uranium alloys.

Table 4 contains a summary of the thermal data obtained. These values have been averaged, both heating and cooling values for the 40 and 60 w/o uranium samples, and the heating and cooling values separately for the 50 and 55 w/o uranium samples. The average values are plotted in Figure 6. A temperature difference of about 14 C between the isotherms on either side of the epsilon phase is indicated with the transformation temperatures gradually increasing across the epsilon phase as the uranium content is increased.

TABLE 4. RESULTS OF COMPARATIVE DIFFERENTIAL THERMAL ANALYSIS ON ZIRCONIUM-40, 50, 55, AND 60 w/o URANIUM ALLOYS

Uranium Content of Alloys in Specimen, w/o	Beginning of Transformation, C	
	Heating	Cooling
40 versus 60 w/o uranium		
40	590	596
60	604	607
50 versus 60 w/o uranium		
50	597	604
60	605	605
40 versus 50 w/o uranium		
40	590	597
50	593	604
50 versus 55 w/o uranium		
50	595	604
55	602	611
55 versus 60 w/o uranium		
55	603	605
60	610	611





Temperature-Gradient Specimens. Examination of a series of specimens containing 40 to 60 w/o uranium annealed under conditions producing a gradient in temperature of about 550 to 650 C over a 5-in. length revealed a two-phase region near the center of the rod consisting of beta and epsilon in all specimens containing 45 to 55 w/o uranium. Typical microstructures obtained from the central portion of such a rod are shown in Figure 7. From thermocouples placed outside the tube containing the specimens, the temperature gradient over the specimen length was determined and the width of the two-phase region with respect to temperature was estimated by metallographic examination. In addition, isotherm temperatures were indicated in the 40 and 60 w/o specimens by the pronounced differences in etching characteristics of the beta and epsilon phases.

The results of these examinations are plotted in Figure 8. While there is some scatter of points, a definite trend is indicated which is substantially the same as that obtained by thermal analysis; that of a gradually increasing temperature of transformation across the epsilon phase with increasing uranium content. The temperature difference between isotherms is 14 C.

An additional check on this temperature difference was obtained from specimens of the 40 and 55 w/o alloys which were annealed together under the same temperature-gradient conditions. The values obtained for the isotherms were 611 and 625 C, respectively. These values are not shown in Figure 8 since they are so high as to suggest some gross error in measurement. However, they do indicate a difference of 14 C between the two isotherms.

Due to temperature-calibration difficulties, the values obtained by this method are believed to be higher than the true values, the thermal analysis values being regarded as more nearly correct.

High-Temperature X-Ray Diffraction. The temperature of transformation of epsilon to beta was determined from the appearance of the X-ray diffraction patterns taken at temperature. The beta phase has its diffraction pattern essentially superimposed upon part of the epsilon pattern. However, by measurement of small shifts in back-reflection lines and observation of relative intensities of epsilon lines to epsilon-plus-beta lines, the presence of both phases could be detected.

The phases identified at temperature are listed in Table 5. Beta and epsilon were found to coexist both on heating up to and cooling down from the beta region. A minimum of about 11 C between the isotherm on either side of the epsilon phase is indicated by these data since the ability to detect small amounts of either beta or epsilon is unknown.

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N29527

N29528

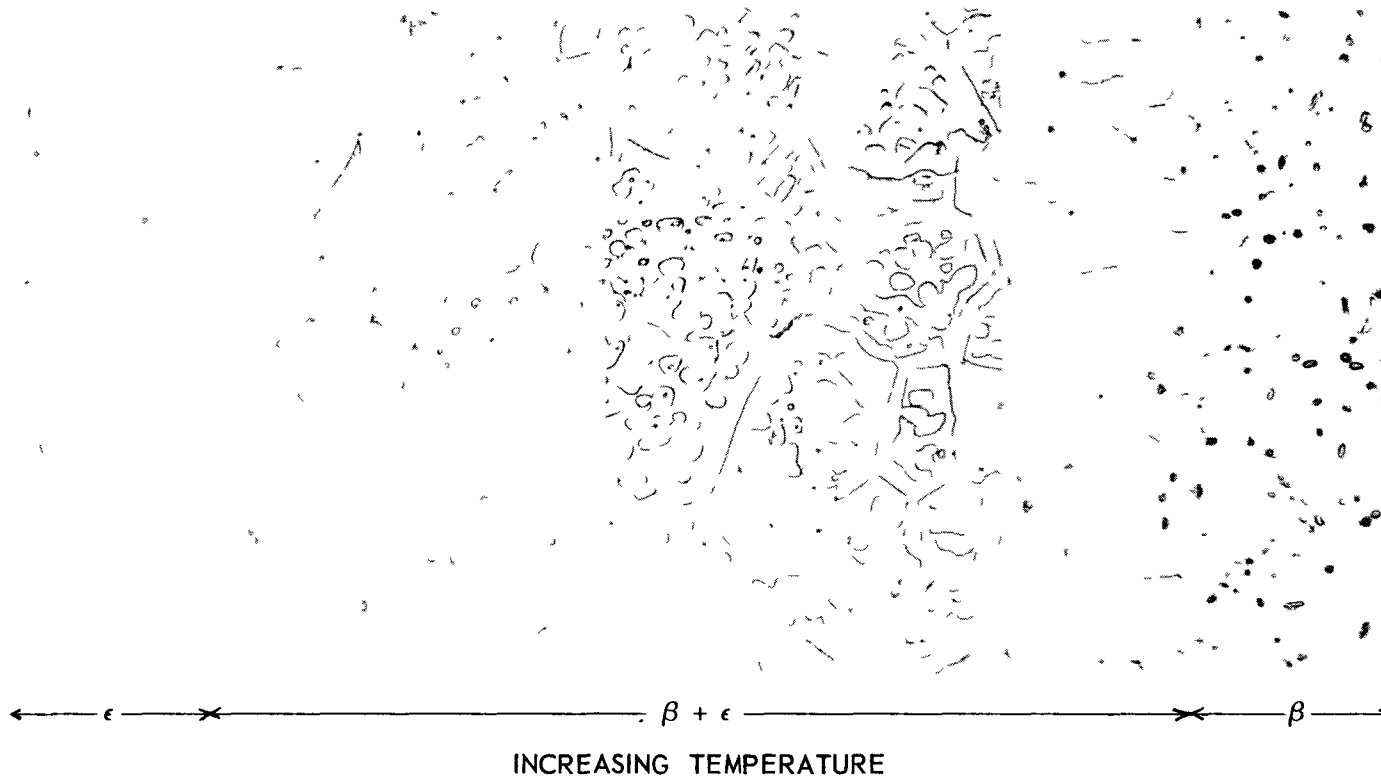
N29529

N29530

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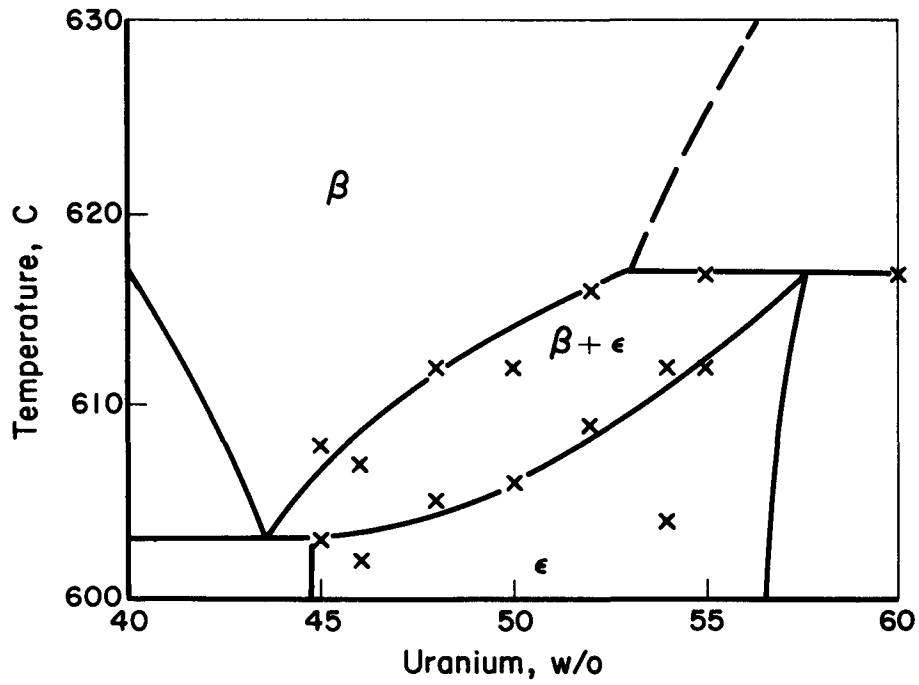
N29533



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**FIGURE 7. MICROSTRUCTURE OF 50 w/o URANIUM ALLOY ANNEALED UNDER CONDITIONS PRODUCING A TEMPERATURE GRADIENT**

APPROXIMATE TEMPERATURE AT SECTION SHOWN: 600 C  
APPROXIMATE GRADIENT OVER SECTION SHOWN: 10 C  
MAGNIFICATION: 500X



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FIGURE 8. THE BETA-PLUS-EPSILON PHASE REGION  
BASED UPON EXAMINATION OF THERMAL-  
GRADIENT SPECIMENS

A marked difference between these results and the results obtained by other techniques is the indicated maximum transformation temperature for the 50 w/o uranium alloy. Since agreement exists between the data obtained both by thermal analysis and by the thermal-gradient technique as to the gradual increase in transformation temperature of the epsilon phase with increasing uranium content, it is felt that the temperature shown for the 50 w/o uranium specimen may be in error as a result of positioning of the thermocouple. This point may bear further study. However, these data do show essential agreement with the data obtained by the other techniques in indicating a small temperature interval for the coexistence of both beta and epsilon.

The alpha zirconium and alpha uranium present in the 45 and 55 w/o uranium alloys, respectively, was produced during the initial heat treatment of the specimen rods, subsequent heating periods in the X-ray camera being insufficient to redissolve these phases to produce equilibrium.

TABLE 5. TEMPERATURES OF THE EPSILON-TO-BETA ZIRCONIUM TRANSFORMATION IN 45, 50, AND 55 w/o URANIUM ALLOY AS DETERMINED IN THE HIGH-TEMPERATURE X-RAY CAMERA

Uranium Content, w/o	Temperature, C	Phases Identified
45	578	$\epsilon + \text{trace } \alpha\text{Zr}$
	583	$\epsilon + \beta + \text{trace } \alpha\text{Zr}$
	588	$\beta + \text{trace } \epsilon + \text{trace } \alpha\text{Zr}$
	604	$\beta + \text{trace } \alpha\text{Zr}$
50	590	$\epsilon$
	594	$\epsilon$
	597	$\beta$
	598	$\beta$
55	579	$\epsilon + \alpha\text{U}$
	583	$\epsilon + \alpha\text{U}$
	587	$\epsilon + \beta + \alpha\text{U}$
	590	$\beta + \text{trace } \epsilon + \alpha\text{U}$
	592	$\beta + \alpha\text{U}$

### Composition Range With Temperature

The composition range of the epsilon region has been estimated upon the basis of metallographic examination of a series of temperature-gradient specimens, ranging in composition from 40 to 60 w/o uranium, and of an additional series of specimens containing 45 to 55 w/o uranium annealed at temperatures of 300, 400, and 550 C.

All specimens containing 45 to 55 w/o uranium, when annealed under conditions producing a gradient in temperature of about 550 to 650 C over a 5-in. length, contained a two-phase region over their central portion. Below this two-phase region, single-phase epsilon was observed, while above this region, beta, with varying amounts of second phase, was found.

The 40 w/o uranium specimen, annealed under the same conditions, did not exhibit this two-phase region, while two 60 w/o specimens, prepared under different conditions, produced different results.

One 60 w/o specimen initially furnace cooled from 800 C and then alternately cold swaged and annealed at 550 C before being annealed in a temperature gradient, exhibited at least two phases over its length, with a three-phase region being produced at the central portion. Since three phases were observed, where normally only two should occur, an additional 60 w/o uranium specimen was annealed at 800 C and water quenched before being annealed under temperature-gradient conditions. This specimen showed only alpha uranium with epsilon and beta over its length with no intermediate two- or three-phase region.

It was therefore concluded that the pretreatment given the first specimen had resulted in precipitation of alpha uranium, thereby enriching the matrix material in zirconium sufficiently to place it in the composition range where the two-phase beta-plus-epsilon region is stable. The 1-week gradient treatment was insufficient to redissolve the uranium and produce a matrix of the intended gross composition. By quenching from 800 C, a homogeneous alloy is produced and equilibrium precipitation of alpha uranium along its length then occurs.

Results obtained with the 40, 45, and 55 w/o uranium alloys were also rechecked after treatment at 800 C followed by a water quench. However, these alloys all showed the same results as were obtained after the initial pretreatment. Upon the basis of these results, as shown in Figure 8, the beta-plus-epsilon region is estimated to extend from about 44 to 57 or 58 w/o uranium.

An additional observation worth noting was made on the 60 w/o uranium specimen. Alpha uranium and beta zirconium or gamma uranium were observed up to a temperature of about 642 C, while above this

temperature only the beta zirconium-gamma uranium solid solution was observed. This provides an additional point on the solubility limit of the alpha-plus-gamma uranium phase region.

Metallographic examination of the series of specimens containing 45 to 55 w/o uranium annealed at temperatures of 300, 400, and 550 C indicates that the epsilon phase extends from about 45 to 53 w/o uranium at 550 C. The 45, 46, 48, 50, and 52 w/o uranium samples all appeared to be essentially single phase after being annealed 8 weeks at 550 C, while the 54 and 55 w/o samples were two phase. The samples annealed for 10 weeks at 300 and 400 C indicated that the 45 w/o sample contained two phases while it was questionable whether the 52 w/o alloy contained one or two phases. The 46 through 50 w/o uranium samples were single phase.

These results indicate that the epsilon phase narrows with decreasing temperature, very rapidly initially on the uranium-rich side and only gradually on the zirconium-rich side.

In an attempt to determine the solubility limits of the epsilon phase more closely, these same specimens were examined by X-ray diffraction methods, along with additional specimens of the 45, 50, and 55 w/o uranium composition which had been annealed for 3 and 4 weeks, respectively, at 550 C. The interplanar spacings of the 50 w/o uranium specimens, annealed for the various periods of time, were found to show greater fluctuations than the variations determined for change in composition from 45 to 55 w/o uranium. This fluctuation in spacings also exceeded the error of measurement. A variation in sharpness of the X-ray lines was also observed.

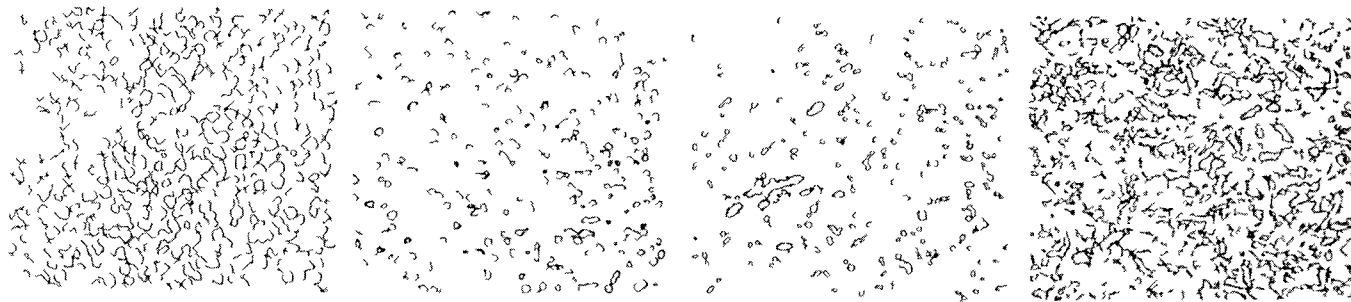
The interplanar spacings of quenched samples were all greater than the values obtained for specimens cooled slowly in the high-temperature X-ray camera. The spacings obtained on quenching may be dependent upon the low-temperature change in rate of lattice expansion of the epsilon phase, the fluctuations reflecting different quenching rates for the various specimens. This low-temperature change is discussed in a later section. Consequently, the room-temperature cell dimensions of epsilon in quenched alloys could not be determined sufficiently well in order to indicate solubility limits.

#### Composition Range With Oxygen

Microstructures of a series of specimens, annealed for 3 weeks at 550 C and containing 45 to 60 w/o uranium, prepared from zirconium of three different oxygen levels are shown in Figure 9. The zirconium used in the preparation of these alloys was: crystal bar zirconium containing about 50 ppm oxygen; normal sponge zirconium containing about 1000 ppm

OXYGEN CONTENT OF ZIRCONIUM ADDITION, w/o

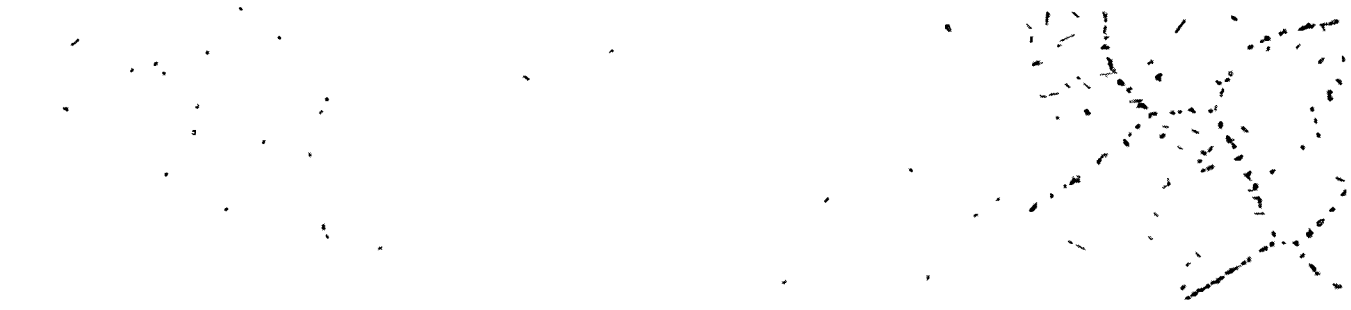
3000 PPM



1000 PPM



50 PPM



COMPOSITION, URANIUM, w/o

45

50

55

60

FIGURE 9. MICROSTRUCTURES OF ZIRCONIUM-45, -50, -55, AND -60 w/o URANIUM ALLOYS CONTAINING VARIOUS AMOUNTS OF OXYGEN

ANNEALED 1 HR AT 800 C AND WATER QUENCHED; ANNEALED 3 WEEKS AT 500 C AND WATER QUENCHED  
MAGNIFICATION: 500X

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oxygen; and sponge zirconium to which oxygen was added to bring its oxygen content up to about 3000 ppm.

It is apparent from these photomicrographs that oxygen drastically constricts the epsilon region and it is concluded that the solubility of oxygen in the epsilon phase is less than 500 ppm. Upon this basis it is also concluded that it is impossible to produce a completely single-phase alloy using sponge zirconium as the base material.

Close metallographic examination of these specimens reveals that alpha uranium and alpha zirconium are present along with epsilon in the 55 and 60 w/o specimens prepared from sponge zirconium containing 3000 ppm oxygen and that these same three phases probably appear in the specimens prepared from normal sponge. It, therefore, appears that maximum solubility of oxygen in the epsilon phase occurs at some point between the 50 and 55 w/o uranium compositions.

Examination of a number of these same alloys in the high-temperature X-ray camera at 575 to 580 C produced essentially the same results and conclusions. Increased amounts of alpha zirconium and alpha uranium in the sponge zirconium-45 and 55 w/o uranium alloys indicated a constricted epsilon region, as did the presence of alpha zirconium in the 50 w/o uranium alloys prepared from sponge containing 3000 ppm oxygen.

The lattice constants of the epsilon phase at 580 C in the 50 w/o uranium alloy were found to have changed as a result of oxygen content. The  $c_0$  value had increased from  $9.212 \pm 0.007$  to  $9.260 \pm 0.003$  A, while  $a_0$  had decreased from  $8.793 \pm 0.002$  to  $8.779 \pm 0.007$  A, between the crystal bar-base and the sponge base containing 3000 ppm oxygen zirconium alloys. These changes in lattice constant are greater than can be accounted for on the basis of uranium enrichment to 55 w/o. Since the 55 w/o uranium alloy made from sponge zirconium has an appreciable amount of alpha uranium present, the oxygen-saturated epsilon phase must contain less than 55 w/o uranium, although more than 50 w/o uranium. The additional shift in lattice parameter therefore indicates some solubility of oxygen in the epsilon phase.

Oxygen was found to have no effect on the temperatures of the isotherms, as indicated by the transformation temperatures determined for the sponge-base zirconium-45 and 55 w/o uranium specimens. The epsilon-to-beta transformation occurred at essentially the same temperatures in these alloys as in the crystal bar-base alloys. However, the 50 w/o uranium specimen prepared from sponge containing 3000 ppm oxygen transformed at the same temperature as the 45 w/o uranium specimen prepared from normal sponge zirconium.

These results further indicate that maximum solubility of oxygen in the epsilon phase occurs at some composition between 50 and 55 w/o uranium.

[REDACTED]

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Alloys which are zirconium rich with respect to this unique composition transform at the lower temperature isotherm, while uranium-rich alloys with respect to this composition transform at the higher temperature isotherm.

### Temperature Dependence of Epsilon-Phase Lattice Parameters

The 50 w/o uranium alloy was studied, during cooling in the high-temperature X-ray camera, in order to determine if changes occur in the epsilon phase at low temperatures. Data were obtained on the 50 w/o uranium alloy prepared from crystal bar zirconium at 580, 480, 380, and 300 C, and at room temperature and on the 50 w/o alloy prepared from sponge zirconium at 580, 480, 380, 280, and 180 C, and at room temperature.

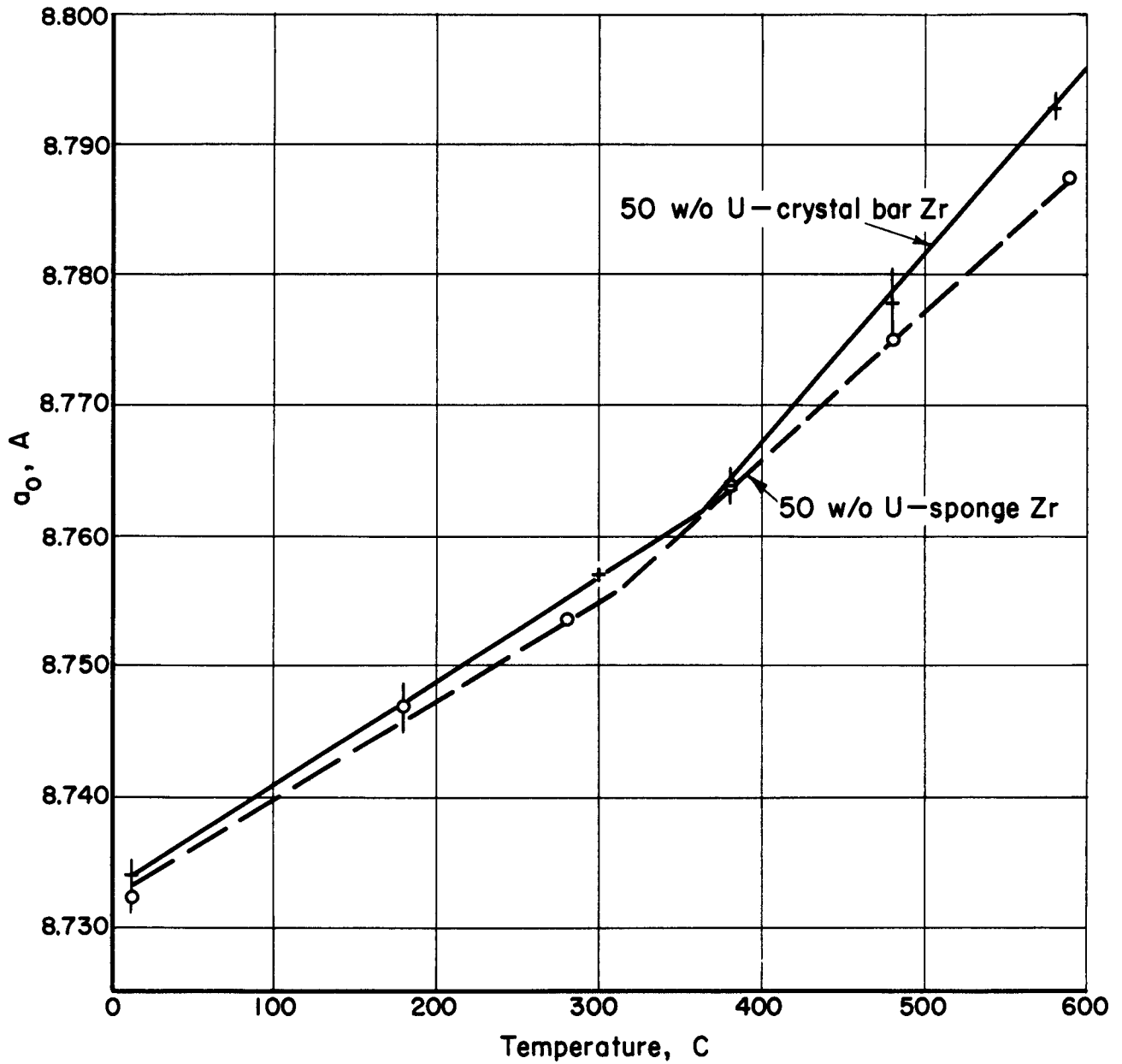
No definite phase changes were observed but the X-ray diffraction patterns obtained at 180 C and room temperature all showed diffuse back reflection lines. Calculated lattice constants, plotted in Figures 10 and 11 indicate a break near 280 C. The change in rate of expansion and the diffuseness of X-ray diffraction lines are indicative of some low-temperature change in the epsilon structure. The nature of this change is uncertain, but it could be a reordering of the epsilon phase, the diffuseness observed being the result of incomplete reaction.

The thermal-expansion coefficient of the beta phase in the crystal bar zirconium-50 w/o uranium alloy was determined to be  $1.54 \times 10^{-5}$  per C from 600 to 712 C by measurement of unit cell dimensions.

### SUMMARY

It has been found possible to form the epsilon phase, by diffusion at 540 C, from uranium and zirconium powders. The ability to form epsilon under these conditions establishes the stability of the epsilon phase. In addition, metallographic high-temperature X-ray and thermal data testify to the stability of the phase.

Epsilon has been found to decompose to alpha zirconium and alpha uranium as a result of its ternary alloy behavior with oxygen and/or nitrogen. With increasing amounts of oxygen, alpha zirconium and alpha uranium first appear in conjunction with the epsilon phase. When sufficient



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FIGURE 10. LATTICE-CONSTANT VARIATIONS OF THE EPSILON PHASE WITH TEMPERATURE

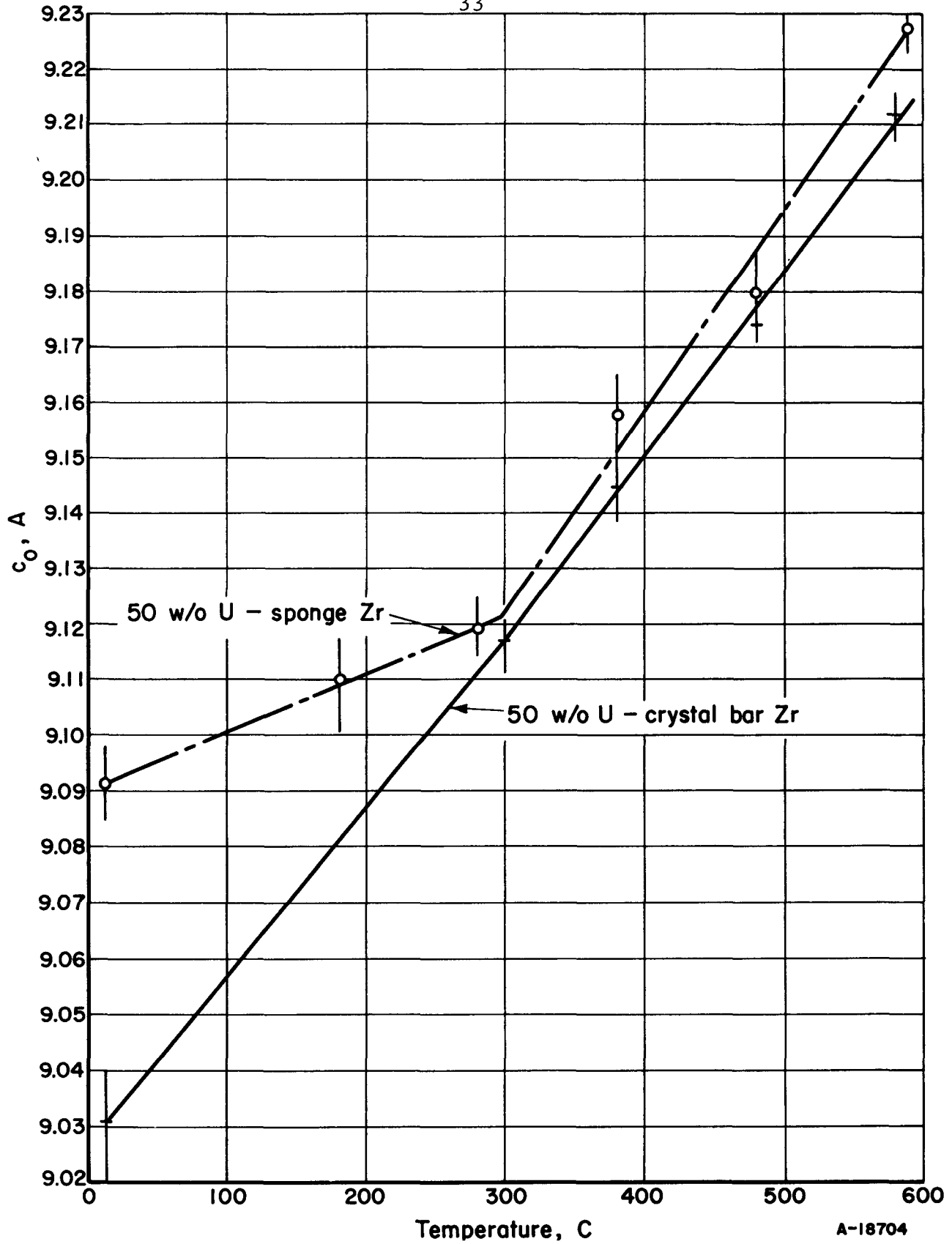


FIGURE 11. LATTICE-CONSTANT VARIATIONS OF THE EPSILON PHASE WITH TEMPERATURE

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oxygen is added, alpha uranium and oxygen-rich alpha zirconium exist together in equilibrium.

Thermal-analysis data and metallographic data, obtained on specimens annealed under conditions producing a gradient in temperature over their length, indicate a temperature difference of 14 C between the isotherms on either side of the epsilon phase. The thermal-analysis data, which are believed to provide the best indication of absolute temperature, show the temperatures of the isotherms to be 593 and 607 C for zirconium-rich and uranium-rich alloys, respectively. High-temperature X-ray data are in substantial agreement as to the difference in temperature between isotherms. However, while the other techniques indicate a gradual increase in temperature of transformation across the epsilon phase, the X-ray data indicate a maximum transformation temperature for the 50 w/o alloy compared with the 45 and 55 w/o alloys.

Upon the basis of metallographic examination of specimens annealed under conditions producing a temperature gradient over their length, the beta-plus-epsilon region is estimated to extend from about 44 to 57 or 58 w/o uranium. Metallographic examination of specimens annealed at lower temperatures indicate that the epsilon region narrows with decreasing temperature; at 550 C the limits are estimated to be about 45 and 53 w/o uranium.

Metallographic examination of a series of epsilon-phase alloys containing various amounts of oxygen indicates that maximum solubility of oxygen in the epsilon phase is less than 500 ppm. These same specimens, as well as high-temperature X-ray data, indicate that maximum solubility of oxygen in the epsilon phase occurs at some composition between 50 and 55 w/o uranium.

A low-temperature modification of the epsilon phase is suspected from the change in rate of lattice expansion of the epsilon phase at low temperatures. This change was observed during cooling in the high-temperature X-ray camera. The nature of this modification is uncertain.

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