The Plutonium-Silicon System

by

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ABSTRACT

The principal characteristics of the plutonium-silicon system include five intermediate phases and three eutectics. The intermediate phases are nominally Pu$_{5-}$Si$_3$ ($\zeta$), Pu$_3$Si$_2$ ($\eta$), PuSi ($\theta$), Pu$_3$Si$_5$ ($\iota$) and PuSi$_2$ ($\kappa$), which melt, respectively, at 1377°, 1441°, 1576°, 1646° and 1638°C, all ± 10°C. Crystal structure data for the intermediate phases are given. The eutectics were found at 3.6 a/o silicon and 590 ± 2°C, between ε-plutonium and $\zeta$; at 54.5 a/o silicon and 1521 ± 10°C, between $\theta$ and $\iota$; and at 83.6 a/o silicon and 1232 ± 5°C, between $\kappa$ and silicon. The solubility of silicon in $\delta$ and ε-plutonium is discussed in detail.
1. INTRODUCTION

Very little information about the plutonium-silicon system has been reported in the literature. Schonfeld et al.\(^1\) and Schonfeld\(^2\) mentioned briefly the existence of five compounds and two of the three eutectics in the system, as a result of early work at Los Alamos. The crystal structure of PuSi\(^8\) has been reported by Ellinger\(^3\), that of \(\sim\) Pu\(_3\)Si\(_5\)\(^4\) by Ellinger\(^3\) and by Runnalls and Boucher\(^4\) and that of \(\sim\) PuSi\(_2\)\(^5\) by Ellinger\(^3\) and by Zachariasen\(^5\).

The detailed phase diagram, as delineated by means of thermal, dilatometric, metallographic and X-ray data, is described and discussed below.

2. EXPERIMENTAL

Plutonium, average purity of 99.96 ± 0.04 w/o, and semiconductor grade silicon were used in the preparation of the alloys. Average values for the chief impurities in the various plutonium stocks used were (in ppm): carbon 215, iron 60, nickel 45, oxygen 50, silicon 65 and thorium 60.

All the specimens were alloyed in an inert atmosphere in an arc melting furnace. Since the weight losses during alloy preparation were so small as to be negligible, the arc cast buttons were not chemically analyzed, and their nominal or weighed out compositions were assumed to be correct. Samples for thermal analysis were prepared by melting the arc cast buttons in either MgO or tantalum crucibles in vacua in an induction furnace.
For heat treatment, each alloy was sealed within an evacuated clear-silica capsule, which in turn was enclosed in a silica tube stoppered with a refractory-wool plug. The outer tube would serve to confine the spread of plutonium contamination should the inner capsule break during heat treatment. The alloys were then placed beside the thermocouples in tube furnaces, which were temperature controlled within ±2°C. The alloys were quenched by plunging the silica tube and its contents into water.

The differential thermal analysis technique was used in obtaining thermal data. Time-versus-temperature and time-versus-differential temperature data were both plotted autographically and simultaneously by means of a two-pen recorder. Chromel-Alumel thermocouples, which had been calibrated against the melting points of high purity NBS aluminum, silver and copper, were used to measure the temperature. The thermal analysis samples were heated and cooled at about 1.5°C/min. in vacua of 10^-4 torr or better.

The dilatometric experiments were performed with autographic strain gauge equipment that has been described by Elliott and Miner. X-ray diffraction specimens for powder photographs consisted of filings contained within clear-silica capillary tubes evacuated to 10^-5 torr. The filings were prepared and loaded into the capillary tubes in a glovebox containing a helium atmosphere. The filings were stress-relieved and water quenched in their evacuated and sealed capillary tubes. These tubes were protected during heat treatment by being enclosed within thin-walled silica sleeves.

Philips powder cameras of 11.46 cm diameter were used in obtaining X-ray data at room temperature, while a high-temperature diffractometer
was used in obtaining data above room temperature. Nickel-filtered copper radiation was used in most of the X-ray work, but a few photographs were obtained with vanadium-filtered chromium radiation. The lattice parameters of the face-centered cubic δ phase were determined by graphical extrapolation of the \( a_0 \) values for the high-angle lines plotted against the Nelson and Riley function.

The metallographic samples were prepared manually in glove boxes using standard methods. Carbon tetrachloride was used as a lubricant in the polishing operations. A 10-second swab etch of 1 part HF, 1 part HNO₃ and 3 parts methanol, by volume, effectively revealed all the microstructures in the plutonium-silicon system. Diamond pyramid hardness measurements at a load of 25 g were obtained from all intermediate phases in the system.

Hilliard and Cahn\(^{(8)}\) have described the systematic point counting method for estimating volume fractions that was used in conjunction with standard metallographic techniques to determine the composition of two of the three eutectics in the system. Since volume percent is not directly proportional to weight percent, a density correction was applied by the method described by C. S. Smith\(^{(9)}\).

A filtration method was used to determine several liquidus values. Silica filtration tubes with silica frits fused in the center were used to contain the molten alloys. The samples were equilibrated at their filtering temperature (within ± 5°C) in vacuum (10⁻⁵ torr) before the liquid was forced through the silica frit by admitting purified helium. The helium was purified by being passed first through a charcoal trap immersed in liquid nitrogen and then through a titanium chip furnace held
at approximately 850°C. The silicon content of the filtrate was determined by a quantitative chemical method.

The melting points of some of the high melting plutonium-silicon alloys were determined by visual observations. The alloys were heated in vacuum on a tungsten wedge, and the temperature at which the alloy became molten was measured optically. The temperature measuring system was calibrated by observing the melting points of high purity gold, silicon and platinum on the tungsten wedge. The melting points all agreed (within 7°C) with the accepted values for these materials. Metallographic examination of some of the plutonium-silicon specimens that had been melted on the tungsten wedge showed no evidence of reaction between the sample and the tungsten. The tungsten wedge method has been described in detail by Olson and Mulford(10).

3. RESULTS AND DISCUSSION

The plutonium-silicon phase diagram, as based on the present work, is shown in Fig. 1. The system is characterized by five intermediate phases, nominally Pu₅Si₃ (ζ), Pu₃Si₂ (η), PuSi (θ), Pu₂Si₂ (ι) and PuSi₂ (κ); by three eutectics and by the slight solubility of silicon in δ, δ' and ε-plutonium.

3.1 Zeta Phase (Pu₅Si₃)

Cramer(11) has determined the crystal structure of ζ phase by single-crystal methods. It has a body-centered tetragonal unit cell containing 4 formula units of Pu₅Si₃. The structure type is that of W₅Si₃, space group I₄/mcm. Lattice parameter measurements made by the powder method
Fig. 1. The plutonium-silicon phase diagram.
WEIGHT PERCENT

1.29 2.85 4.80 7.26 10.52 14.98 21.52 31.97 51.40

THERMAL ANALYSIS
OBSERVED MELTING
FILTRATION
DIFFRACTOMETRY
DILATOMETRY
LATTICE SPACING
SINGLE PHASE
TWO PHASE

1646°C
1576°C
1521°C
1377°C
1232°C ±5°C

LIQUID

54.5% Si
83.6% Si

83.6% Si

51.40

50
40
30
20
10
0

0 10 20 30 40 50 60 70 80 90 100

ATOMIC PERCENT SILICON

TEMPERATURE, °C

1800 1600 1400 1200 1000 800 600 400 200 0

0

Pu 0.2% Si

31.97

3.6% Si

497°C ±3°C

312°C ±3°C

212°C ±5°C

135°C ±4°C

497°C ±3°C

312°C ±2°C

212°C ±5°C

135°C ±4°C

590°C ±2°C
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with CrKα radiation indicate that the compound has a narrow homogeneity range. The lattice parameters of the zeta phase in a slowly cooled 33 a/o silicon alloy were \( a = 11.385 \pm 0.005 \) and \( c = 5.443 \pm 0.003 \) Å, whereas an arc-cast 37 a/o silicon alloy, which had essentially a single-phase microstructure (see Fig. 2), had lattice parameters of \( a = 11.407 \pm 0.005 \) and \( c = 5.444 \pm 0.003 \) Å. The latter dimensions lead to a calculated density of \( 12.00 \pm 0.02 \) g cm\(^{-3}\).

Zeta melts peritectically at 1377° ± 10°C, as determined by observing the melting of a 37 a/o silicon alloy, and has a hardness in the range between 350 and 490 DPH.

3.2 Eta Phase (Pu\(_3\)Si\(_2\))

Eta was found by powder diffraction data to belong to space group P\(\bar{4}\)/mm and to have the primitive tetragonal \( \text{U}_2\text{Si}_2 \) type of structure and 2 formula units in the unit cell. The lattice parameters of \( \text{Pu}_3\text{Si}_2 \) coexisting with small proportions of \( \text{Pu}_5\text{Si}_3 \) and \( \text{PuSi} \) in an arc-cast 40 a/o silicon alloy (Fig. 3) were determined with CrKα radiation to be \( a = 7.483 \pm 0.002 \) and \( c = 4.048 \pm 0.002 \) Å. These parameters lead to a calculated density of 11.33 g cm\(^{-3}\). The photomicrograph of an equilibrated 40 a/o silicon alloy (Fig. 4) shows essentially single phase eta.

Eta has a hardness value of about 660 DPH. The peritectic temperature, 1441° ± 10°C, was determined by the tungsten wedge method with a 40 a/o silicon alloy that had been heat treated at 840°C.

3.3 Theta Phase (PuSi)

On the basis of X-ray powder data obtained with a 50 a/o silicon alloy and CuKα radiation, theta was found to be orthorhombic and isostructural.
with USi and ThSi. The structural type is that of FeB, and the space group is Pnmm. There are 4 formula units in the unit cell, which has the dimensions \( a = 5.727 \pm 0.005 \), \( b = 7.933 \pm 0.003 \) and \( c = 3.847 \pm 0.001 \) Å. The calculated density is 10.15 g cm\(^{-3}\). The Widmanstätten structure observed in an arc-cast 50 a/o silicon alloy (see Fig. 5) suggests that the compound may have a high temperature homogeneity range.

An arc-cast 50 a/o silicon alloy melted congruently at 1576° ± 10°C on the tungsten wedge. Theta has a hardness in the range between 600 to 1000 DPH.

3.4 Iota (\( \sim \text{Pu}_2\text{Si}_5 \))

The crystal structure of the \( \iota \) phase, as determined by X-ray powder data, has been reported by Ellinger\(^{(3)}\) and by Runnalls and Boucher\(^{(4)}\) to be of the hexagonal \( \text{AlB}_2 \) type, but silicon deficient. In both references a composition of approximately 60 a/o silicon is reported but the lattice parameters given for the hexagonal unit cell differed as follows:

\[
\begin{align*}
\text{Ellinger:} & \quad a = 3.876 \pm 0.002, \quad c = 4.090 \pm 0.002 \text{ Å}; \\
\text{Runnalls and Boucher:} & \quad a = 3.884 \pm 0.003, \quad c = 4.082 \pm 0.003 \text{ Å}.
\end{align*}
\]

The present work, however, indicates that the homogeneity range of \( \iota \) does not extend to 60 a/o silicon. As shown in Fig. 6, the microstructure of an arc-melted 60 a/o silicon alloy has an appreciable amount of interdendritic \( \theta \) phase and after homogenization at 840°C for 1000 hr the microstructure was essentially unchanged. There was a small amount of \( \theta \) present in a 63 a/o silicon alloy but a 63.5 a/o silicon alloy consisted entirely of \( \iota \) phase. The unit cell dimensions of \( \iota \) were found to be \( a = 3.875 \pm 0.004 \) and
c = 4.102 ± 0.007 Å, which lead to a calculated density of 8.96 ± 0.04 g cm⁻³ as compared to the measured density of 9.03 g cm⁻³.

3.5 κ (~ PuSi₂)

Zachariasen(5) was the first to identify the κ phase, and did so by means of the powder pattern of a plutonium-silicon sample of unknown composition. He found that κ had the tetragonal ThSi₂ type of structure with lattice parameters of a = 3.98 ± 0.01 and c = 13.58 ± 0.05 Å. Later, Ellinger(3) reported the lattice parameters of the κ phase in an alloy containing excess silicon to be a = 3.967 ± 0.001 and c = 13.72 ± 0.03 Å.

Kappa was found to have a homogeneity range and, as the silicon content of kappa decreased, the tetragonal structure was found to deform to an orthorhombic structure. The X-ray powder pattern (CuKα radiation) of a 64.5 a/o silicon arc-melted alloy resembled that of the tetragonal κ phase, except for a general broadening and splitting of the lines that was suggestive of a slightly distorted unit cell of the ThSi₂ type. Similar patterns were obtained for specimens containing 65 and 66 a/o silicon, but split lines were not observed in the pattern of a 66.7 a/o silicon alloy. The broadened and split lines were resolved in the powder patterns when chromium radiation was used. These lines were indexed on the basis of body-centered orthorhombic unit cells having dimensions as shown in Table 1. It is expected that the

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Lattice Parameters of κ* (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/o Si</td>
<td>a</td>
</tr>
<tr>
<td>64.5</td>
<td>3.988</td>
</tr>
<tr>
<td>65.0</td>
<td>3.978</td>
</tr>
<tr>
<td>66.0</td>
<td>3.973</td>
</tr>
<tr>
<td>66.7</td>
<td>3.968</td>
</tr>
</tbody>
</table>

* The compositions of κ are unknown.
orthorhombic structure will prove to be isostructural with the orthorhombic rare-earth "disilicides" reported by Perri et al. (12).

As shown in Table 1, the b/a ratio goes from 0.992 at 64.5 a/o silicon to unity at 66.7 a/o silicon. However, the microstructures of these alloys showed that only the 64.5 a/o silicon alloy was single phase κ. The rest of the alloys (65.0, 66.0 and 66.7 a/o Si) contained increasing amounts of the κ/Si eutectic (see Fig. 7). Homogenization of these alloys at 980°C for 1100 hr resulted in no perceptible dissolution of the eutectic silicon. The compositions of the κ phase in those alloys are, therefore, unknown, but it is evident that stoichiometric PuSi₂ is not attained when the κ phase becomes tetragonal. To date there is no evidence that the orthorhombic and tetragonal structures correspond to different phases.

3.6 Crystallization of the λ and κ phases.

The reactions of the λ and κ phases with the liquid phase were not conclusively established in the present investigation. The phases that were observed in the arc-melted alloys in the composition range of 63 to 66 a/o silicon are listed in Table 2. The 64 a/o silicon alloy was the only one

<table>
<thead>
<tr>
<th>Composition, a/o Si</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.0</td>
<td>λ + trace θ</td>
</tr>
<tr>
<td>63.5</td>
<td>λ + trace (κ ?)</td>
</tr>
<tr>
<td>64.0</td>
<td>κ + λ</td>
</tr>
<tr>
<td>64.5</td>
<td>κ</td>
</tr>
<tr>
<td>65.0</td>
<td>κ + trace (eutectic ?)</td>
</tr>
<tr>
<td>66.0</td>
<td>κ + κ/Si eutectic</td>
</tr>
</tbody>
</table>
composed of \( \iota \) and \( \kappa \), the \( \iota \) phase being present in a layer across the bottom of the button (see Fig. 8). The melting temperatures of the \( \iota \) and \( \kappa \) phases, as determined by the tungsten wedge method, in arc-cast alloys containing 63.5 and 65.5 a/o silicon, were found to be 1646° and 1638°C, respectively. The hardness values for \( \iota \) and \( \kappa \) were in the ranges 680-860 and 420-505 DPH.

3.7 Eutectics and Liquidus

The composition of the plutonium-rich eutectic \( (L = \epsilon - Pu + \zeta) \) was found by metallography to be 3.6 ± 0.3 a/o silicon. The eutectic temperature was found to be 590° ± 2°C*, on the basis of differential thermal analysis (DTA) of seven specimens having compositions between 2.5 and 20 a/o silicon. The eutectic composition was difficult to locate, since the specimens that were examined apparently undercooled sufficiently to precipitate both primary \( \epsilon \)-plutonium and \( \zeta \) (see Fig. 9), but the DTA and the filtration data both lend some support to the choice of composition.

The composition of the eutectic that occurs between \( \theta \) and \( \iota \) was found to be 54.5 ± 0.5 a/o silicon. This composition was determined first by volume fraction analysis and was then confirmed by the usual metallographic techniques (see Fig. 10). The eutectic temperature, 1521° ± 10°C, was determined by visual melting point observations using the tungsten wedge method on a 55 a/o silicon alloy that had been heat treated at 850°C.

* Limits placed on the temperature of an isotherm determined by DTA are mean deviations.
The composition of the silicon-rich eutectic \((L = \kappa + Si)\), 83.6 ± 0.2 a/o silicon, was determined by volume fraction analysis and was confirmed by the usual metallographic techniques (see Fig. 11). The eutectic temperature, 1232° ± 5°C, was determined both by DTA and by visual melting point observations. The values obtained by the two methods agreed within 4°C.

Very few liquidus points were determined in the present investigation, and, as a result, most of the liquidus is shown as a broken line in Fig. 1. However, the liquidus lying between 0 and 3.6 a/o silicon in the diagram was determined by DTA, and that portion indicated as a solid line above 3.6 a/o silicon was determined by filtration.

3.8 Plutonium Allotropes

There appears to be very little solubility of silicon in \(\alpha\), \(\beta\) or \(\gamma\)-plutonium since the addition of silicon to plutonium has very little effect on the transformation temperatures of these allotropes. The average transformation temperatures for the allotropes, as determined by high-temperature X-ray diffractometry and dilatometry are \(\alpha = \beta = 135^\circ\text{C}\) and \(\beta = \gamma = 212^\circ\text{C}\).

The \(\delta\)-phase solvus was determined by the lattice-spacing method. Although the solution of silicon in the \(\delta\) phase does not stabilize it to room temperature, it can be retained in a metastable state at room temperature if the alloys are cooled at a sufficiently rapid rate from the \(\delta\) phase. In the case of the X-ray samples, the alloy filings, contained in evacuated silica capillary tubes, were plunged into water.
The alloy filings containing 0.5 a/o silicon transformed partially to α phase when quenched from 450°C while those filings containing 0.75 a/o silicon or more retained the metastable δ phase. Therefore, under the quenching conditions used, slightly more than 0.5 a/o silicon was necessary to retain the δ phase to room temperature. Since it is known that cold work, such as is produced by filing action, causes the metastable δ phase to transform to α phase, then it could be expected that the stresses set up during the quench would promote the transformation of the δ phase at the borderline composition of 0.5 a/o silicon.

The alloys that were homogenized at 350°C and quenched also transformed partially to α phase, thus indicating that the solubility limit of silicon in δ phase at 350°C is about 0.5 a/o silicon which agrees with the extrapolated δ-phase solvus shown in Fig. 1.

Listed in Table 3 are homogenizing treatments given the arc-cast buttons and the lattice parameters of the δ phase obtained with filings that were stress relieved for either 5 or 10 minutes at the homogenizing temperatures, and then quenched.

The lattice parameter/composition relationships of the δ solid solution, shown in Fig. 12, are based on two experimental points, one at 0.5 and the other at 0.75 a/o silicon, and on the value for pure δ plutonium, as obtained by the extrapolations to 0% solute of the linear lattice parameter/composition curves of the aluminum and cerium δ solid solutions. (13, 14)

The δ-phase lattice parameter should have a constant value in all two-phase δ + ζ alloys homogenized at the same temperature. However, as shown
Table 3
Alloy Heat Treatments and 8-Phase Lattice Parameters

<table>
<thead>
<tr>
<th>Nominal Comp. (a/o Si)</th>
<th>Temp. (°C)</th>
<th>Time at Temperature (hr)</th>
<th>8-Phase Lattice Parameter (A)</th>
<th>No. of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>450</td>
<td>1260 - 2750</td>
<td>8 + α</td>
<td>4.6326 ± 0.0003</td>
</tr>
<tr>
<td>0.75</td>
<td>465</td>
<td>600 - 600</td>
<td>8</td>
<td>4.6295 ± 0.0004</td>
</tr>
<tr>
<td>0.75</td>
<td>450</td>
<td>1030 - 2870</td>
<td>8</td>
<td>4.6299 ± 0.0001</td>
</tr>
<tr>
<td>0.75</td>
<td>400</td>
<td>1560 - 2750</td>
<td>8 + ζ</td>
<td>4.6320 ± 0.0001</td>
</tr>
<tr>
<td>0.75</td>
<td>350</td>
<td>1280 - 1280</td>
<td>8 + ζ (+α)</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>465</td>
<td>600 - 600</td>
<td>8 + ζ</td>
<td>4.6276 ± 0.0002</td>
</tr>
<tr>
<td>1.0</td>
<td>450</td>
<td>1030 - 2870</td>
<td>8 + ζ</td>
<td>4.6288 ± 0.0002</td>
</tr>
<tr>
<td>1.0</td>
<td>400</td>
<td>1560 - 2750</td>
<td>8 + ζ</td>
<td>4.6315 ± 0.0001</td>
</tr>
<tr>
<td>1.0</td>
<td>350</td>
<td>1280 - 1280</td>
<td>8 + ζ (+α)</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>450</td>
<td>1030 - 2870</td>
<td>8 + ζ</td>
<td>4.6282 ± 0.0003</td>
</tr>
<tr>
<td>2.0</td>
<td>400</td>
<td>1560 - 2750</td>
<td>8 + ζ</td>
<td>4.6306 ± 0.0002</td>
</tr>
<tr>
<td>2.0</td>
<td>350</td>
<td>1280 - 1280</td>
<td>8 + ζ (+α)</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>485</td>
<td>1050 - 2150</td>
<td>8 + ζ</td>
<td>4.6252 ± 0.0001</td>
</tr>
<tr>
<td>5.0</td>
<td>450</td>
<td>1030 - 1030</td>
<td>8 + ζ</td>
<td>4.6275 ± 0.0001</td>
</tr>
</tbody>
</table>

(a) All the alloy buttons were held at 450°C for at least 1030 hr before the final heat treatment at the temperature and for the time listed in the table.

(b) The uncertainty is the standard deviation.
Fig. 12. Lattice parameter/composition relationships.
in Fig. 12, there is a systematic decrease in the lattice parameter values as the silicon content increases, i.e., as the proportion of ζ phase increases. The smallest values that were obtained at each temperature, corresponding to the largest proportion of silicon in solution, have been taken to represent the solubility limits (see Table 1). The spread in the lattice parameter values at each temperature corresponds to about 0.1 a/o silicon, which is within the estimated uncertainty (0.1 to 0.2 a/o Si) of the solubility determinations. Microstructural confirmation of the X-ray results is shown in Fig. 13 wherein a very small proportion of ζ phase still exists in the δ matrix of a 1 a/o silicon alloy after the homogenizing treatments at 450° and 465°C.

Delta phase is formed peritectoidally, ε-Pu + ζ = δ, at 497° ± 3°C. It decomposes eutectoidally, δ-Pu = γ-Pu + ζ, at 312° ± 3°C (see Fig. 14). The peritectoid temperature was determined only by DTA, whereas the eutectoid temperature was determined by DTA, dilatometry and high-temperature X-ray diffraction work.

The δ/(δ + ε) boundary was determined by dilatometry and by DTA.

R. O. Elliott(7) has shown by high-temperature diffractometry that as little as 0.25 a/o silicon eliminates the δ' phase in plutonium-silicon alloys.

A 5 a/o silicon alloy was homogenized in the ε + ζ field at 550°C for 500 hr. When filings from this alloy were quenched from 550°C, the ε-phase transformed to δ-phase which had a lattice parameter of a = 4.6319 Å. According to the lattice parameter/composition curve shown in Fig. 12, this value corresponds to 0.6 a/o silicon in solution in the δ-phase, which should also represent the solubility limit of silicon in ε-phase at 550°C.
The maximum solubility of silicon in $\varepsilon$ phase can be determined roughly by extrapolating the $\varepsilon/(L + \varepsilon)$ boundary, as determined by DTA, to its intersection with the eutectic isotherm. This extrapolation gives the maximum solubility as 1 a/o at 590°C. An extrapolation of the $(\delta + \varepsilon)/\varepsilon$ boundary indicates that the solubility of silicon in $\varepsilon$ phase at 497°C is 0.5 a/o.

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REFERENCES


3) F. H. Ellinger, Ibid., Chap. 25.


11) D. T. Cramer, Los Alamos Scientific Laboratory, unpublished data.


Fig. 2. Pu - 37 a/o Si alloy, as cast, essentially single-phase $\zeta$. 
100X

Fig. 3. Pu - 40 a/o Si alloy, as cast, showing primary $\theta$ (light) surrounded by peritectic $\eta$ (grey) and $\zeta$ (dark). 
500X

Fig. 4. Pu - 40 a/o Si alloy, heat treated at 840°C for 1080 hr and quenched, essentially single phase $\eta$. 
500X

Fig. 5. Pu - 50 a/o Si alloy, as cast, essentially single-phase $\theta$, showing Widmanstätten precipitate. 
500X
Fig. 6. Pu - 60 a/o Si alloy, as cast, showing primary \( \nu \) with interdendritic \( \Theta \) (light phase), the highly oriented microcracks that can be seen in \( \nu \) are characteristic of this phase. 500X

Fig. 7. Pu - 66.7 a/o Si, heat treated at 840°C for 1080 hr and quenched, consisting principally of \( \kappa \) with a slight amount of \( \kappa/\text{Si} \) eutectic. 500X

Fig. 8. Pu - 64 a/o Si alloy, as cast, appears to be massively segregated with \( \kappa \) (light phase) across the top and \( \iota \) (dark phase) near the bottom. 500X

Fig. 9. Pu - 4 a/o Si alloy, as cast, showing both primary \( \zeta \) (light phase) and primary Pu (light gray) with eutectic (dark gray). 500X
Fig. 10. Pu - 54.1 a/o Si alloy, as cast, showing primary $\theta$ and $\theta/\gamma$ eutectic. 500X

Fig. 11. Pu - 83.6 a/o Si alloy, as cast, consisting essentially of $\kappa/Si$ eutectic 500X

Fig. 13. Pu - 1 a/o Si alloy, after heat treatment at 450 and 465°C, showing a very small amount of $\zeta$ in a matrix of $\delta$-Pu. 500X

Fig. 14. Pu - 2.5 a/o Si alloy, slow cooled, showing the $\gamma/\zeta$ eutectoid in the coarse $\epsilon/\zeta$ eutectic. 1000X