A contribution to the study of
the uranium-silicon equilibrium diagram

by
H. VAUGOYEAU, L. LOMBARD and J.P. MORLEVAT

Translation by
M.A. FERADAY

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A CONTRIBUTION TO THE STUDY OF THE URANIUM-SILICON EQUILIBRIUM DIAGRAM*

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Translation by M.A. Feraday

ABSTRACT

The authors have defined the character of the uranium-silicon equilibrium phase diagram in the compositional region between 50 and 70 at.% silicon. They have determined the single phase regions relating to the phases USi, U₃Si₅, USi₁₈₈ and shown the peritectic nature of the first and the last of these compounds. The hexagonal phase U₃Si₅ is a congruent melting compound. A new tetragonal crystalline structure, a uranium monosilicide, has also been found.

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Contribution à l'étude du diagramme
d'équilibre uranium-silicium*

par

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Résumé

Les auteurs ont précisé l'allure du diagramme
d'équilibre uranium-silicium dans le domaine de composition
compris entre 50 et 70 atomes pour cent de silicium. Ils
ont déterminé les domaines monophasés relatifs aux phases
USi, U$_3$Si$_5$, USi$_{1,88}$ et montré la nature péritectique du
premier et du dernier de ces composés. La phase U$_3$Si$_5$
hexagonale est à fusion congruente. Une nouvelle structure
cristalline, quadratique, du monosiliciure d'uranium a, en
outre, été mise en évidence.

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Chalk River, Ontario

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INTRODUCTION

The data on the uranium silicon system are relatively old and often contradictory (1,2,3) in particular in the compositional area between Si/U ratio of 0.7 to 2.0.

Besides, our own studies on this phase diagram, or ternary systems which are based on it, have permitted us to observe many anomalies in the properties of these alloys (4,5).

These facts have led us to attempt a systematic study of this part of the uranium-silicon diagram. The research has been done on one hand on the properties of the compounds themselves (stoichiometry, structure), on the other hand on the relationship of phases (as outlined by the equilibrium diagram). We maintain this plan in our report.
Finally, each of the sections will be traditionally divided into description of experimental methods, then listing and interpretation of results.

A  STUDY OF PHASES

Our research has been carried out on the three compounds in the compositional region of concern, i.e., USi, U₃Si₅, USi₁₈₈. Certain authors (3) have in addition pointed out the existence of a hexagonal USi₂ compound, but a recent study (5) has shown that it was really a ternary compound with a formula U₆Si₁₁O.

I  Experimental Techniques

a) Preparation and Heat Treatment

1. Preparation

We have used the technique already employed in our laboratory (6,7) of direct synthesis by high frequency melting under an atmosphere of purified argon and in a water cooled mold.

The alloys have all been prepared from solid electrolytic uranium and very pure silicon powder.

We have therefore been able to obtain samples containing less than 50 ppm carbon and 200 ppm oxygen. In addition, the final composition obtained was very close to the theoretical target composition by the addition of a very slight excess (50 mg for 100 g of sample) of silicon; the excess is required to compensate for the slight silicon evaporation during melting.

2. Heat Treatment

We have used a high frequency induction heated vertical setup already described (7).

* Note. We have adopted the nomenclature of Brown & Norreys. U₃Si₅ designates the hexagonal compound USi₂₋ₓ and USi₁₈₈ the tetragonal compound USi₂₋ₓ. 
We have always heat-treated under an atmosphere of static argon, purified by a getter, and in a tungsten crucible. The quenching effect was obtained by blowing helium at the end of the run.

b) **Analytical Methods**

The main objective was to find out for each of the three phases existing (USi, $U_3Si_5$, $USi_{1.88}$) its behaviour as a function of the temperature: stability and stoichiometry.

In addition, for the USi, a study of the crystalline structure has been necessary.

In order to resolve these different problems we have used either high temperature analytical methods, or means of studying at room temperature samples quenched or not quenched.

1) **Method of Analyzing at High Temperature**

We have been able by means of a high temperature X-ray diffraction apparatus, built and tested in an adjacent laboratory, to study from $300^\circ C$ to $1600^\circ C$ the relationships between the two-phase alloy region USi-$U_3Si_5$ on one part and $USi_{1.88}$-$USi_3$ on the other part.

The interpretation of the diagram obtained permits the identification of different phases at a given temperature, and therefore, to study as a function of temperature, the stability of the compounds of interest.

2) **Means of Investigation at Room Temperature**

These examinations have been done mainly on the two-phase alloys $U_3Si_2$ - USi, USi - $U_3Si_5$, and $USi_{1.88}$ - $USi_3$, previously treated for some hours at $1000^\circ C$, $1250^\circ C$ and $1550^\circ C$, then quenched.

The character of the different phases present was determined by X-ray techniques.

Their composition was calculated starting with silicon analysis using an electron microprobe.
These investigations have permitted in particular the study of the composition limits of the different phases in equilibrium at high temperature.

We have, in addition, made up some diffusion couples to study the formation of the higher silicides (U₃Si₅ and USi₁.₈₈).

The components of the couple, previously polished were put in a molybdenum crucible, closed by a piston of the same metal. The assembly was then placed in the vice press already used in a previous study (7).

Keeping the temperature for some hours at 1000°C, 1250°C and 1500°C after sealing was sufficient to assure that the couple was in equilibrium.

We have therefore been able to verify firstly that U₃Si₅ forms starting with USi + USi₁.₈₈ at all temperatures and secondly the same for USi₁.₈₈ starting with U₃Si₅ + USi₃. The different phases were identified by X-ray analysis after completely crushing the couple.

Note that the optical microscope has been used very little in this study other than as a means of control. In fact the identification of phases by this method, at least for the higher silicides, is practically impossible.

II RESULTS

First we will report the USi results, then those relating to the hexagonal compound U₃Si₅, finally, we describe the properties of the tetragonal compound USi₁.₈₈.

a) The Compound USi

It occurred to us very quickly that, if there really exists a phase corresponding to the formula USi, the compound does not have the structure described by Zachariasen, but a tetragonal structure. Regarding the structure described by Zachariasen it corresponds in fact to a ternary compound with a formula U₈Si₈O. A complete crystallographic study on this topic is being prepared for publication in our laboratory (9).
All these experiments show that the phase USi exists in equilibrium with $\text{U}_3\text{Si}_2$ in one region of the phase diagram - and with $\text{U}_3\text{Si}_5$ in another region at ambient temperature to 1500°C. The measured values of the compositional limits of this phase at different temperatures are summarized in Table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>Two-Phase Region</th>
<th>Ratio Si/U - Limit At</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td>$\text{U}_3\text{Si}_2$ - USi</td>
<td>1.03</td>
</tr>
<tr>
<td>USi - $\text{U}_3\text{Si}_5$</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The phase USi seems then to possess a narrow single phase region (0.3 at% silicon).

These results show, besides a very slight hyperstoichiometry in relation to the theoretical composition of USi.

b) **The Hexagonal Compound $\text{U}_3\text{Si}_5$**

1) **Stability**

The experiment shows that the phase $\text{U}_3\text{Si}_5$ exists in equilibrium with USi between room temperature and 1600°C.

2) **Stoichiometry**

The experimental data relative to the stoichiometry of $\text{U}_3\text{Si}_5$ at the temperatures studied are shown in Table 2.

**TABLE 2**

<table>
<thead>
<tr>
<th>Two-Phase Region</th>
<th>Ratio Si/U - Limit At</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td>$\text{U}_3\text{Si}_5$ - USi</td>
<td>1.72</td>
</tr>
<tr>
<td>$\text{U}_3\text{Si}<em>5$ - USi$</em>{1.88}$</td>
<td>1.78</td>
</tr>
</tbody>
</table>
Concerning the $U_3Si_5 + USi_{1.88}$ region it is necessary to note that it is very difficult to prepare two-phase samples in this region. The corresponding Si/U ratio lies between 1.78 and 1.79.

In addition, it is not possible to distinguish between $U_3Si_5$ and $USi_{1.88}$ other than by X-ray techniques. The limiting value given for $U_3Si_5$ in this region corresponds to an alloy with the highest Si/U ratio still showing the hexagonal structure.

The two-phase region $U_3Si_5 - USi_{1.88}$ is therefore very limited in composition, whereas the maximum width of the single phase $U_3Si_5$ is 0.8 at% silicon.

In the temperature range studied, the composition limit of the solid solution of the phase studied varied little; it remains slightly higher than the value (1.67) corresponding to the formula $U_3Si_5$ presented by Brown and Norreys.

c) The Tetragonal Compound $USi_{1.88}$

1) Stability

Our studies have shown the stability of $USi_{1.88}$ in equilibrium with $USi_3$ in all temperature regions studied from room temperature to 1500°C.

2) Stoichiometry

Table 3 summarizes the results obtained concerning the variation of this parameter as a function of temperature.

<table>
<thead>
<tr>
<th>Two-Phase Region</th>
<th>Ratio Si/U - Limit At</th>
<th>1000°C</th>
<th>1250°C</th>
<th>1500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$USi_{1.88} - U_3Si_5$</td>
<td>1.79</td>
<td>1.79</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>$USi_{1.88} - USi_3$</td>
<td>1.84</td>
<td>1.84</td>
<td>1.84</td>
<td></td>
</tr>
</tbody>
</table>

The width of the single phase region of the phase of interest is near 0.7 at% silicon.
The compositional limits of this solution varied little as a function of the treatment temperature.

The relevant observation on the U₃Si₅ - USi₁.₈₈ region remains valid; we have taken as the lower limit of the solid solution USi₁.₈₈ the lowest Si/U ratio corresponding to an alloy which is almost single phase containing only the tetragonal USi₁.₈₈ phase.

d) Conclusions

**Compound USi:** This tetragonal compound exists in equilibrium with U₃Si₂ and U₃Si₅ in all the temperature ranges examined. The width of the single phase region is fairly narrow (0.₃ at%) and does not vary with temperature. It is very slightly hyper-stoichiometric as compared with the composition of USi.

**Phases U₃Si₅ and USi₁.₈₈:** These two compounds although very close in composition have different crystalline structures and co-exist in all the temperature ranges studied.

In addition, each of these compounds possess: A single phase region of notable width (0.₈ at% silicon), roughly independent of temperature at least up to 1500°C. Finally our measures of the high temperature composition of these phases (USi₁.₇₁ for U₃Si₅ and USi₁.₈₃ for USi₁.₈₈) are in good accord with the values of Brown and Norreys: USi₁.₆₇ and USi₁.₈₈ respectively.

### B. LAYOUT OF THE LIQUIDUS CURVES

#### I. Operational Method

We have carried out the determination of the temperatures of the start and finish of melting of different alloys prepared by the method described in A I.

The samples were placed in a tantalum boat and laid upon alloy fragments of a composition identical to theirs.

Their heating was done by means of the apparatus already used for the heat treatment. Each alloy underwent several successive tests, of several minutes at increasing temperatures in
20°C steps. It was examined after each holding step. We have therefore analyzed a series of alloys of different compositions varying from USi$_{0.8}$ to USi$_{2.0}$.

II. Results

Table 4 summarizes the results obtained. We specify in the first place that we have called start of melting the temperature at which the angles of the sample started to become round (appearance of the first liquid) and the end of melting the temperature where the sample slumped completely (disappearance of the last solid).

<table>
<thead>
<tr>
<th>Ratio Si/U</th>
<th>Phases Present When Cold</th>
<th>Start of Melting (± 10°C)</th>
<th>End of Melting (± 10°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USi$_{0.8}$</td>
<td>USi - U$_3$Si$_2$</td>
<td>1540°C</td>
<td>1590°C</td>
</tr>
<tr>
<td>USi$_{0.85}$</td>
<td>USi - U$_3$Si$_2$</td>
<td>1540°C</td>
<td>1540°C</td>
</tr>
<tr>
<td>USi$_{1.02}$</td>
<td>USi</td>
<td>1580°C</td>
<td>1600°C</td>
</tr>
<tr>
<td>USi$_{1.5}$</td>
<td>USi - U$_3$Si$_5$</td>
<td>1590°C</td>
<td>1750°C</td>
</tr>
<tr>
<td>USi$_{1.70}$</td>
<td>Hexagonal U$_3$Si$_5$</td>
<td>1770°C</td>
<td>1770°C</td>
</tr>
<tr>
<td>USi$_{1.75}$</td>
<td>Hexagonal U$_3$Si$_5$</td>
<td>1750°C</td>
<td>1765°C</td>
</tr>
<tr>
<td>USi$_{1.80}$</td>
<td>Tetragonal USi$_{1.88}$</td>
<td>1710°C</td>
<td>1760°C</td>
</tr>
<tr>
<td>USi$_{1.85}$</td>
<td>Tetragonal USi$_{1.88}$</td>
<td>1710°C</td>
<td>1750°C</td>
</tr>
<tr>
<td>USi$_{1.90}$</td>
<td>USi$_{1.88}$ + traces</td>
<td>1710°C</td>
<td>1740°C</td>
</tr>
</tbody>
</table>

Conclusions

Examination of these results requires some comments. We are going to discuss them by breaking them into three series of alloys in order of increasing Si/U ratio.
1) **Si/U Ratio = 0.8 to 0.85**

Phases present: $U_3Si_2 - USi$

The alloy $USi_{0.85}$ melts suddenly at a constant temperature. It shows in addition (Fig. 1) an almost perfect eutectic appearance with a slight excess of $U_3Si_2$. The melting range of the alloy $USi_{0.80}$ extends from $1540^\circ$ to $1590^\circ$C. We therefore have a eutectic $U_3Si_2 + USi$ melting at $1540^\circ$C to a composition close to $USi_{0.85}$.

2) **Si/U Ratio Between 1 to 1.5 Inclusive**

Phases present: $USi$ and $U_3Si_5$

All these alloys show the start of melting at a constant temperature of $1580^\circ$C and the finish of melting at a temperature increasing from 1600 for $Si/U = 1$ to 1750$^\circ$C for $Si/U = 1.5$. It appears that the compound $USi$ decomposes peritectically at $1580^\circ$C ± 10$^\circ$C.

3) **Si/U Ratio Between 1.70 to 1.90 Inclusive**

The alloy with a composition $USi_{1.70}$ shows all the characteristics of a congruent melting compound: identical temperatures for the start and finish of melting, i.e., $1770^\circ$C.

In turn when the $Si/U$ ratio goes from 1.70 to 1.90 the temperature for the end of melting moves steadily from 1770 to 1740$^\circ$C while the temperature for the start of melting goes down at first progressively from 1770 to $1710^\circ$C and then remains at that value. It stays constant for the $Si/U$ ratios present between 1.80 and 1.90. This last composition interval corresponds to the presence of the tetragonal $USi_{1.88}$ as the major phase in these alloys.

These facts allow us to conclude that contrary to previous data (1) the hexagonal compound is a congruent melting phase, and the tetragonal compound is peritectic in nature.

In summary the compound $USi$ decomposes in a peritectic manner at $1580^\circ$C ± 10$^\circ$C according to the reaction

$$USi \rightarrow U_3Si_5 + \text{liquid}$$
It forms with U₃Si₂ a eutectic melting at 1540°C ± 10°C and with a composition USi₀.₈₅.

The hexagonal phase U₃Si₅ is a congruent melting compound melting at 1770°C ± 10°C and giving on cooling by a peritectic reaction formation of the tetragonal phase USi₁₈₈.

This reaction occurs at 1710°C ± 10°C and is written

\[ U₃Si₅ + \text{liquid} \rightarrow USi₁₈₈ \]

C GENERAL CONCLUSIONS

These experimental results given above, allow us to propose the following conclusions, which are summarized in Fig. 2.

Fig. 2b shows on a larger scale the region of the uranium-silicon system that we have studied in detail.

The compound USi with a tetragonal structure decomposes at 1580°C ± 10°C according to the following peritectic reaction:

\[ USi \rightarrow U₃Si₅ + \text{liquid} \]

In addition, it forms with U₃Si₂ a eutectic possessing the following characteristics:

- Melting Point: 1540°C ± 10°C
- Composition: USi₀.₈₅ (≈46 at% silicon)

It exists in a region which is independent of temperature and which has a width of 0.3 at% silicon.

The phase U₃Si₅ is a compound with a hexagonal structure melting in a congruent manner at 1770°C ± 10°C.

On the other hand, it exists in a single phase region which does not vary with temperature and with a maximum width of 0.₈ at% silicon.
The tetragonal compound USi$_{1.88}$ decomposes peritectically at 1710°C ± 10°C according to the reaction:

$$\text{USi}_{1.88} \xrightarrow{\Delta} \text{U}_3\text{Si}_5 + \text{liquid}$$

The width of its region of existence (0.7 at% silicon) does not vary in a sensitive manner with temperature.

REFERENCES

FIGURE 1

$U_3Si_2$ - Eutectic

$U_3Si_2$ - Light Grey

USi - Dark Grey
FIGURE 2 URANIUM SILICON EQUILIBRIUM DIAGRAM
FIGURE 2b  PARTIAL EQUILIBRIUM DIAGRAM FOR THE URANIUM SILICON SYSTEM