

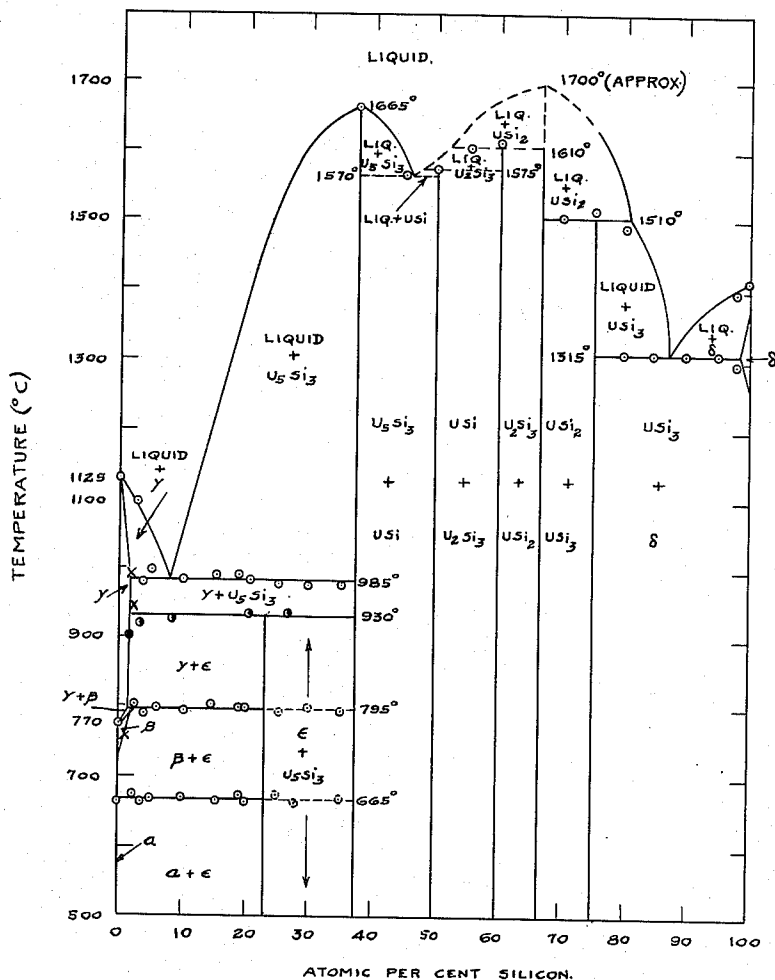
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URANIUM-SILICON ALLOY AND PROCESS OF PRODUCING SAME

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URANIUM-SILICON PHASE DIAGRAM.

- - THERMAL ARREST OBTAINED ON HEATING.
- X - TWO-PHASE ALLOY BY MICROSCOPIC EXAMINATION.
- - ONE-PHASE ALLOY BY MICROSCOPIC EXAMINATION.
- ① - EPSILON PERITECTOID TEMPERATURE.

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URANIUM-SILICON ALLOY AND PROCESS OF PRODUCING SAME

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The present invention relates to alloy compositions and, more particularly, to novel compositions of uranium and silicon, and to a process for preparing the same.

Uranium structures have the disadvantage of being readily corroded by water. It is therefore an object of the present invention to provide a uranium alloy that retains the good qualities of uranium metal but which at the same time is relatively corrosion resistant.

It is a further object of the present invention to provide novel alloy compositions containing uranium and silicon.

It is another object of this invention to provide a new alloy of uranium and silicon which has low corrosion characteristics.

The present invention also contemplates the provision of a novel uranium-silicon alloy suitable for coating uranium.

A further object of this invention is to provide a new process for preparing uranium-silicon alloys of excellent corrosion characteristics.

Other objects and advantages of the invention will be apparent from the following description taken in conjunction with the accompanying drawing, wherein:

Fig. 1 is a phase diagram of the uranium-silicon system.

According to the present invention, alloys of uranium and silicon are prepared by melting solid uranium and silicon powder in alundum crucibles lined with beryllia, using an evacuated induction furnace. In the preparation of most of the alloys, the heating current can be induced directly in the uranium which forms the major portion of the charge. However, when making the high silicon alloys it is necessary to heat the charge by heat transfer from a graphite sleeve surrounding the crucible, due to the high electrical resistivity of silicon.

On the basis of thermal, microscopic and X-ray studies of the alloys with varying proportions of uranium and silicon, a complete equilibrium phase diagram has been prepared as shown in Fig. 1. Referring to this diagram, it will be seen that there are six intermediate phases in the uranium-silicon alloy system, five of which melt or undergo peritectic decompositions at temperatures above 1500° C., while the sixth, which may be designated as epsilon (ϵ), decomposes by a peritectoid reaction at a much lower temperature, say about 930° C. In the solid state, neither metal is soluble in the other to any large extent and the melting point of either metal is lowered by the addition of the other.

Beginning at the uranium side of the diagram, it can be seen that the addition of silicon lowers the melting point of uranium from 1125° C. to the eutectic temperature of 985° C. when 9 atomic per cent of silicon is present. The liquidus then rises steeply to 1665° C., the melting point of an alloy of the composition U_5Si_3 . The exact shape and location of the various liquidus curves in Fig. 1 are approximate.

The solid solubility of silicon in uranium has also been investigated by microscopic examination of alloys containing 1.0 atomic per cent and 2.5 atomic per cent of

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silicon, quenched from various temperatures. These quenching experiments have shown that the maximum solid solubility in the gamma (γ) uranium region of Fig. 1 is about 1.75 atomic per cent silicon at 980° C. and, in the beta (β) uranium region, less than 1.0 atomic per cent silicon at 750° C. The fact that the temperature of the alpha (α) to beta solid transformation in pure uranium is not changed by the addition of silicon indicates that the solubility of silicon in alpha uranium is negligibly small.

Regardless of the quenching temperature, the uranium-rich phase is alpha uranium, for X-ray diffraction has shown that it is not possible to retain the beta or gamma forms in these alloys by quenching. Careful examination of photomicrographs of as-melted ingots in the composition range 0 to 37.5 atomic per cent silicon shows that the alloys formed are not in a condition of stable equilibrium since a third phase is evident as a rim or shell around the primary dendrites. This phase is epsilon and it contains about 23 atomic per cent of silicon and is formed by a peritectoid reaction between gamma uranium and U_5Si_3 at a temperature of about 930° C. to about 945° C.

Epsilon, however, forms so sluggishly that samples of these alloys from unannealed ingots may be said to be in a state of metastable equilibrium. In fact, examination of such samples by thermal analysis and X-ray diffraction does not disclose the presence of epsilon. The temperature of the alpha to beta transformation in pure uranium, 665° C., is not changed by the addition of silicon. The temperature of the beta to gamma transformation in pure uranium, however, is raised from 770° C. to 795° C. as shown by the phase diagram in Fig. 1. Both of these transformations, the alpha to beta and the beta to gamma, are found in metastable alloys containing up to 37.5 atomic per cent of silicon, as shown by the dotted lines in Fig. 1. No thermal arrest is obtained at 930° C. Similarly, examination of these metastable alloys by X-ray diffraction shows only the presence of alpha uranium and U_5Si_3 .

However, if alloys in the range of 0 to 37.5 atomic per cent of silicon are annealed to a condition of stable equilibrium, epsilon forms and the phase relations correspond to the full lines of Fig. 1. At temperatures below 930° C., alloys containing less than 24 atomic per cent of silicon contain a uranium-rich phase and epsilon, while alloys with more than this amount of silicon contain epsilon and U_5Si_3 . Since stable alloys containing from 23 to 37.5 atomic per cent of silicon do not contain any uranium-rich phase at temperatures below 930° C., the solid transformations at 665° C. and 795° C. do not occur in these alloys.

The equilibrium temperature of the peritectoid reaction by which epsilon forms has been determined by using alloys with a fairly large grain size produced by normal furnace cooling from the liquid state. The method for determination of the equilibrium temperature comprises a determination of the temperature at which epsilon begins to form on slow cooling. This formation temperature is obtained by microscopic examination of specimens of the same alloy quenched at regular temperature intervals during the cooling process. The first appearance of a peritectoid rim of epsilon around particles of U_5Si_3 fixes the epsilon formation temperature between fairly close limits, and it is possible to estimate the temperature at which the reaction begins from the thickness of the epsilon rim.

It has been found that the presence of carbon as an impurity in small amounts up to 0.10 weight per cent markedly lowers the peritectoid temperature by as much as 80° to 90°, and it is therefore desirable to employ alloys containing a minimum of carbon when determin-

ing the true equilibrium temperature of the peritectoid reaction. Using an alloy having an average carbon content of about 0.01 per cent by weight, photomicrographs show that, for an alloy containing 20 atomic per cent of silicon, epsilon formation begins to occur at some temperature between about 956° C. and about 939° C. An estimated average epsilon formation temperature for alloys containing about 3.5 to about 37.5 atomic per cent of silicon is about 940° C., the temperature being somewhat lower in alloys of low silicon content. It is believed that even traces of carbon can lower the peritectoid temperature when the silicon content is also low.

The epsilon decomposition temperature for these alloys should be the same as the formation temperature under equilibrium conditions and, when determined by examination of quenched samples of slowly heated substantially completely epsilonized alloy, is estimated at about 910° C., which is some 30° lower than the formation temperature determined by slow cooling. This depression of the temperature may be due to local segregation of the small amount of carbon in the alloy, thereby producing regions having lower epsilon decomposition temperatures because of slightly higher carbon content. In general, the best value for the temperature of the epsilon peritectoid reaction is judged to be about 930° C., as shown in the phase diagram of Fig. 1.

Alloys containing epsilon are best prepared by chill casting a melt of the desired composition, thus producing a fine-grained structure, and then heat treating the cast alloy at temperatures of about 750° C. to about 850° C. to allow the reaction between uranium and U_5Si_3 to occur. The crystal structure of epsilon is given as tetragonal with $a_1=6.017$ Å and $a_3=8.679$ Å. There are 12 uranium and 4 silicon atoms to the unit cell which would correspond to the formula U_3Si . The composition of epsilon derived from microscopic examination is 23.0 ± 0.5 atomic per cent of silicon (i. e., 3.40 ± 0.10 per cent of silicon by weight). This composition corresponds roughly to the formula $U_{10}Si_3$.

The determination of the phase equilibria in the range 37.5 atomic per cent to 66.7 atomic per cent of silicon is complicated by the high melting points and extreme brittleness of the phases involved. X-ray evidence shows the existence of four intermediate phases in this composition range, viz., U_5Si_3 , USi , U_2Si_3 , and USi_2 . The compound U_5Si_3 melts sharply at 1665° C. and shows no thermal effects below this temperature. The high temperature region of the phase diagram between U_5Si_3 and USi_2 shows a melting point of almost 1700° C. for USi_2 and is known only approximately, as indicated by the dotted lines in Fig. 1. USi enters into an eutectic reaction with U_5Si_3 at about 1570° C. and then undergoes peritectic decomposition at about 1575° C. One product of the peritectic decomposition of USi is U_2Si_3 , which in turn undergoes peritectic decomposition at about 1610° C. One product of the peritectic decomposition of U_2Si_3 is USi_2 which melts at a temperature in the neighborhood of 1700° C. At the silicon end of the system USi_3 forms by a peritectic reaction at about 1510° C. and enters into a eutectic reaction with delta (δ), the silicon-rich solid solution, at about 1315° C., the melting point of the silicon employed being 1420° C.

USi_3 has the Cu_3Au type of crystal structure, being simple cubic with uranium atoms at 000 and silicon atoms at $0\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $1\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $2\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The lattice parameter is 4.03 Angstrom units, the calculated density 8.23 grams per cubic centimeter and the measured density 8.11 grams per cubic centimeter. The compound USi_3 decomposes peritectically at 1510° C. to give USi_2 and a liquid containing about 82 atomic per cent of silicon. USi_3 and delta silicon form a eutectic alloy melting at about 1315° C. at a composition of about 86 atomic per cent silicon.

To summarize, the uranium-silicon alloy system is composed of the following solid phases:

- (1) Alpha uranium, stable up to 665° C., and containing a negligible amount of silicon in solid solution;
- (2) Beta uranium, stable between 665° C. and 770°–795° C., depending on composition, and containing less than 1 atomic per cent of silicon in solution;
- (3) Gamma uranium, stable between 770°–795° C. and 1125° C., its melting point, which forms an eutectic with U_5Si_3 at 985° C. and contains about 1.75 atomic per cent of silicon in solid solution at this temperature;
- (4) Epsilon, which forms by a peritectoid reaction between gamma uranium and U_5Si_3 at 930° C. and contains 23 atomic per cent silicon;
- (5) U_5Si_3 , which melts at 1665° C. and forms an eutectic with USi at 1570° C.;
- (6) USi , which forms by a peritectic reaction between liquid and U_2Si_3 at 1575° C.;
- (7) U_2Si_3 , which forms by a peritectic reaction between liquid and USi_2 at 1610° C.;
- (8) USi_2 , which melts at approximately 1700° C., and has a body-centered tetragonal crystal structure;
- (9) USi_3 , which forms by a peritectic reaction between USi_2 and liquid at 1510° C., and which forms an eutectic with delta silicon at 1315° C.; and
- (10) Delta silicon, which contains very little uranium in solid solution and melts at 1420° C.

Uranium-silicon alloys containing more than 30 atomic per cent of silicon are extremely brittle and easily broken. Because of this alloys containing more than 30 atomic per cent of silicon are of comparatively small utility.

The most useful of the binary uranium-silicon alloys are those containing from 15 to 25 atomic per cent of silicon which have been heat treated so that a high proportion of the alloy has been converted to the epsilon phase. Epsilon is an intermediate phase in the uranium-silicon system containing about 23 atomic per cent of silicon. This phase forms by means of a peritectoid reaction whose temperature is lowered by the presence of carbon. Investigation of the corrosion resistance of epsilon in various media shows that epsilon is quite superior to pure uranium metal and many other uranium alloys. The epsilon phase is a high strength alloy which possesses some degree of ductility.

In forming a binary uranium-silicon alloy containing from 15 to 25 atomic per cent of silicon and having a high proportion of the alloy in the epsilon phase, it is important to convert the melt to an alloy having a fine grain size. Such a fine-grained alloy may be produced by chill casting the melt into a copper or a graphite mold. The alloy constituents, uranium and silicon, are melted in a graphite crucible, arranged for bottom pouring, in an evacuated induction furnace. When the alloy is completely molten and well mixed, it is poured through the bottom of the crucible into a copper mold. The temperature of the copper mold is not sensibly above that of the room, so that a chill casting in vacuo is obtained, giving an alloy in the desired fine-grained condition. Very fine-grained alloys may also be obtained by a liquid quench technique in which the completely molten alloy is quenched immediately in cold water.

This fine-grained alloy should then be annealed in vacuo or in an inert atmosphere for at least 10 hours at a temperature between 700° C. and 850° C. To insure that conversion to the epsilon phase is substantially complete, it is ordinarily desirable to continue the heat treatment for at least approximately 16 hours. The optimum temperature range for annealing runs from 750° C. to 800° C. For alloys in which the presence of small amounts of carbon as an impurity has lowered the peritectoid temperature at which the epsilon phase forms, it is preferable to carry out the annealing at temperature below 800° C. Since the epsilon phase is substantially softer than the corresponding cast structure, it is possible to make use of hardness measurements in studying the formation of the

epsilon phase which takes place during the annealing operation. The epsilon phase forms by a peritectoid reaction between the uranium matrix and U_5Si_3 . The production of the epsilon phase in an alloy results in an increase in its density. The amount of epsilon phase produced reaches a maximum for alloys containing from 20 to 25 atomic per cent of silicon.

Binary uranium-silicon alloys which contain from 15 to 25 atomic per cent of silicon and which have been heat treated to convert a high proportion of the alloy to the epsilon phase have corrosion resistant properties which are far superior to those of metallic uranium. Structures made from such alloys stand up much better than uranium structures when they are placed in direct contact with water. Structures made from the epsilon alloy appear to be from 500 to 1,000 times more corrosion resistant in boiling water containing 2 parts per million of chloride ion than similar structures made from pure uranium metal. Uranium corrodes quite rapidly in distilled water at 100° C. Binary uranium-silicon alloys containing from 15 to 25 atomic per cent of silicon which have not been heat treated to transform a high proportion of the alloy to the epsilon phase corrode almost as rapidly as pure uranium in distilled water at 100° C. This is probably due to the fact that the chill cast alloy which has not been heat treated has a uranium matrix which is very susceptible to corrosion. The binary uranium-silicon alloys which have been heat treated possess a continuous matrix of the epsilon phase. The binary uranium-silicon alloys containing from 15 to 20 atomic per cent of silicon which have been heat treated to transform them into the epsilon phase corrode only slightly during the first 100 hours in water at 100° C., and thereafter substantially no corrosion occurs even though the test is continued for 500 hours. Similar binary alloys containing from 20 to 25 atomic per cent of silicon show substantially no corrosion in distilled water at 100° C. even after 500 hours. In order to obtain good corrosion resistance in these alloys, it is important to anneal the chill cast alloys for a minimum of 16 hours in order to secure substantially complete transformation of the alloy to the epsilon phase. The corrosion of these alloys in water does not seem to be appreciably affected by the presence of 2 to 5 parts per million of chloride ion in the water or by bubbling air, hydrogen, or oxygen through the water for long periods of time. A film or coating of an oxide nature apparently forms on epsilon alloys during corrosion in water and serves to protect the alloy from further corrosion. No noticeable galvanic corrosion occurs when epsilon alloys are placed in contact with silver, aluminum, beryllium, copper, lead, zinc, tin, nickel, monel or stainless steel in boiling distilled water. These epsilon phase alloys have been tested in a steam autoclave at a pressure of 125 pounds per square inch (178° C.) and have been found to corrode only slightly faster under these conditions than in boiling distilled water. Carbon impurities have no effect upon the corrosion resistance of the epsilon phase alloys.

Controlled tests were run in which solid cylinders of pure uranium and of an epsilon phase binary uranium-silicon alloy were placed in aluminum jackets which were pinholed and heated in a steam autoclave at a pressure of 125 pounds per square inch. The uranium cylinder failed after 2 hours while the cylinder of epsilon phase alloy showed no noticeable changes after 16 days of treatment in the autoclave.

A solid cylinder of epsilon alloy containing 15 atomic per cent silicon was completely enclosed in an aluminum jacket. A #80 hole was drilled through the jacket to produce a leak. This cylinder was found to swell only about 5 mils on the diameter after 90 days in boiling water; whereas a similarly tested cylinder of uranium developed swellings 80 mils high in three days. Likewise, a jacketed cylinder of pure epsilon (about 25 atomic per cent silicon) when pin-holed and tested in steam at 178°

C. for 31 days showed only some localized swelling while a similarly treated cylinder of uranium failed in two hours.

A 25 atomic per cent silicon specimen of epsilon appears to resist oxidation at 200° C. in air for an indefinite time while pure uranium oxidizes quickly in air at 100° C. A similar specimen of epsilon alloy is not attacked by hydrogen at 325° C. after 4 hours of heating while pure uranium disintegrates into a fine powder in 20 minutes at 225° C. in hydrogen.

The density of binary uranium-silicon alloys containing from 15 to 25 atomic per cent of silicon which have been heat treated to convert the alloy to the epsilon phase decreases from a value somewhat greater than 16.5 grams per cubic centimeter at 15 atomic per cent silicon to a value somewhat less than 15.5 grams per cubic centimeter at 25 atomic per cent silicon. The density of these binary alloys as cast is slightly less than the corresponding alloy after heat treatment to convert the alloy to the epsilon phase. An alloy containing 23 atomic per cent of silicon which has been converted to the epsilon phase has a density of 15.45 grams per cubic centimeter.

Whereas binary uranium-silicon alloys containing from 15 to 25 atomic per cent of silicon as cast have a hardness of 40 or greater on the Rockwell "C" scale, the same alloys after heat treatment to convert them to the epsilon phase are much softer and have a hardness between 25 and 30 on the Rockwell "C" scale.

Stress-strain data indicate that the yield point in compression for binary uranium-silicon alloys containing from 15 to 25 atomic per cent of silicon which have been heat treated to convert the alloy to the epsilon phase appears to be about 125,000 pounds per square inch and is apparent after a 0.5 to 1 per cent reduction in length. The ultimate strength lies roughly at about 275,000 pounds per square inch, and the total reduction in length prior to breaking is between 12 and 16 per cent. Alloys with the lowest silicon content have the highest yield point and the greatest over-all plasticity. Cast uranium-silicon alloys which have not been heat treated to convert them to the epsilon phase have a high yield point but are comparatively brittle and fail with very little deformation.

Hot compression data on an epsilon phase alloy containing 23 atomic per cent of silicon show that the yield point and compressive strength decrease rapidly from 600° C. to 850° C. The yield strength at 600° C. is 55,000 pounds per square inch, and it decreases to 18,000 p. s. i. at 700° C. The yield strengths at 750° C. and at 850° C. are 10,000 p. s. i. and 4,000 p. s. i. respectively. The low values of compressive strength in the 750° to 850° C. range show that the epsilon alloy has a fair amount of ductility at these temperatures.

A binary alloy of uranium and silicon which has been heat treated to convert it to the epsilon phase may be extruded if care is taken to completely sheath the billet of epsilon alloy in copper tubing. The copper sheath serves to lubricate the die and to prevent any oxidation of the epsilon billet. It is important to carry out the extrusion at a temperature lying in the range of 750° to 800° C. At temperatures lower than about 750° C. the epsilon alloy possesses insufficient ductility to be readily extruded. At temperatures greater than 800° C. there is a tendency for the epsilon alloy to revert back to a finely divided mixture of uranium phase and U_5Si_3 . Since the peritectoid temperature at which the epsilon phase is in equilibrium with gamma uranium and U_5Si_3 is markedly lowered by the presence of small amounts of carbon impurities in the alloy, it is necessary to rigidly control the temperature of extrusion so that the epsilon alloy will be sufficiently ductile but not heated above its decomposition temperature. Epsilon alloys are soft enough to be threaded and machined in various other ways.

Although the present invention has been described with respect to particular illustrative examples and embodiments, it will be understood that variations and modifications may be made and equivalents substituted therefor

without departing from the principles and true spirit of the invention. Such variations and modifications are believed to be within the scope of the present specification and within the purview of the appended claims.

I claim:

1. A process of making a soft, ductile and corrosion resistant article from a binary alloy of uranium and silicon containing from 15 to 25 atomic per cent of silicon which comprises chill casting the article from a melt of said alloy and then heat treating the cast article for at least ten hours at a temperature between 700° and 850° C.

2. The epsilon phase of a binary alloy of uranium and silicon characterized as having a tetragonal crystal structure with $a_1=6.017$ Å and $a_3=8.679$ Å and having 12 uranium and 4 silicon atoms to the unit cell, and having a silicon content of $23.0 \pm$ atomic per cent, and formed

by a peritectoid reaction between gamma uranium and U_5Si_3 at 930° C.

3. A corrosion resistant binary alloy of uranium and silicon containing from 15 to 25 atomic percent of silicon wherein the normally brittle intermetallic compounds of uranium and silicon are present in the relatively soft and ductile epsilon phase.

4. A corrosion resistant binary alloy of uranium and silicon containing from 20 to 25 atomic percent of silicon wherein the normally brittle intermetallic compounds of uranium and silicon are present in the relatively soft and ductile epsilon phase.

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