UNCLASSIFIED

CT-3309

METALLURGY AND CERAMICS

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

UNITED STATES ATOMIC ENERGY COMMISSION

ALLOYS OF URANIUM AND SILICON. II. THE EPSILON PHASE

By
Gust Bitsianes

CT-3309

Price \$ 0.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

This document is
PUBLICLY RELEASABLE

Hugh Kincer *H. Kincer*
Authorizing Official
Date *11/28/06*

June 1945

Massachusetts Institute of Technology
Cambridge, Massachusetts

Technical Information Service Extension, Oak Ridge, Tenn.

CLASSIFICATION CANCELLED

DATE FEB 16 1957

For The Atomic Energy Commission

H. R. Canale
Chief, Declassification Branch

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

II
~~CONFIDENTIAL~~

CT-3309

Massachusetts Institute of Technology

Contract No. W-7405-eng-175

ALLOYS OF URANIUM AND SILICON

II. THE EPSILON PHASE

By

Gust Bitsianes

June 1945

Manuscript Received: November 5, 1945
Report Received: November 15, 1945
Figures Received: November 19, 1945

Date Issued: November 27, 1945

-iii-iv-

~~CONFIDENTIAL~~

SECRET

~~CONFIDENTIAL~~

CT-3309

ALLOYS OF URANIUM AND SILICON
II. THE EPSILON PHASE*

Work done by: A. R. Kaufmann, B. D. Cullity, Gust Bitsianes,
and M. Neher

Written by: Gust Bitsianes

ABSTRACT

Epsilon is an intermediate phase in the uranium-silicon system containing about 23 atomic per cent 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 and possesses some degree of ductility. These properties indicate a distinct possibility of using epsilon in direct contact with cooling water.

1. Introduction

One of the purposes for studying the uranium-silicon system was to find possible alloys which might be used as a pile material. In this respect the alloys had to meet certain requirements, including high resistance to corrosion and good metallic properties. It was found that of all the phases isolated in the uranium-silicon system, the epsilon phase best fulfilled these requirements. This phase is the lowest silicon compound in the system, containing about 3.40 weight per cent silicon. Preliminary tests revealed that epsilon has a good corrosion resistance and some degree of ductility. These considerations implied the need for the detailed investigation which comprises this paper.

*Contribution from the Metallurgical Project, Massachusetts Institute of Technology. Based on Reports CT-3060, May, 1945; CT-2997, Apr., 1945; CT-2780, Feb., 1945; CT-2699, Jan., 1945; CT-2619, Dec., 1944; CT-2472, Nov., 1944; and CT-2387, Oct., 1944.

~~CONFIDENTIAL~~

2. Effect of Carbon on the Epsilon Equilibrium

The epsilon equilibrium⁽²⁾ consists of a peritectoid reaction at 930°C. It has been found, however, that small amounts of carbon up to 0.10 weight per cent materially affect the equilibrium conditions - in some cases lowering the peritectoid temperature as much as 100°C. The idea of a ternary system involving carbon was previously suspected from attempts to fix the equilibrium temperature by means of long-time anneals. The alloys used contained 0.05 to 0.10 weight per cent carbon and ended up as three phase, equiaxed structures which appeared to be at equilibrium. Further evidence in this direction was noted when the three phase equilibrium attributed to carbon was approached from two directions. Here, cast and "epsilonized" samples of the same alloy attained the three-phase equilibrium after a long anneal at 830°C.

In order to study the effect of carbon quantitatively, a series of alloys was made containing 20 atomic per cent silicon with varying carbon content. The carbon ranged from 0.01 to 0.14 weight per cent and was added to the charge in the form of graphite.

A suitable procedure for studying the slow epsilon transformation has been outlined⁽²⁾ and was used exclusively in this particular study. Accordingly, the results obtained on each alloy are listed in Table 1 along with estimated values for epsilon formation and decomposition temperatures. A series of photomicrographs illustrating the establishment of epsilon formation and decomposition temperatures is shown in Fig. 2 and 3.

When the estimated epsilon formation and decomposition temperatures were plotted against the respective carbon contents, the curves in Fig. 1 were obtained. This figure may be looked upon as a section of the uranium-silicon-carbon ternary diagram on a constant silicon plane, and it can be seen that carbon tends to suppress the peritectoid some 80° to 90°C at its higher concentrations. The results on the high-carbon alloy were carefully checked by anneals approaching equilibrium conditions (15 to 20 hours) and the 80°C suppression was confirmed. It should be noted that the pure epsilon peritectoid temperature can be extrapolated

TABLE 1

MICROCONSTITUENTS ON HEAT-TREATING U-Si-C ALLOYS

U - Uranium
 Code: C - Compound, U_5Si_3
 E - Epsilon

Alloy Number	PE-1	PE-5	PE-3	PE-2
<u>Analyses</u>				
Silicon (Atomic per cent)	20.0	20.3	19.1	20.5
Silicon (Weight per cent)	2.86	2.92	2.70	2.96
Carbon (Weight per cent)	0.010	0.023	0.069	0.133
<u>Temperatures, °C</u>				
	<u>Slow Cooling</u>			
956	U-C 940°C	U-C	U-C	U-C*
939	U-C-E	U-C	U-C	U-C
928	U-C-E	U-C 915°C	U-C	U-C
906	---	U-C-E	U-C	U-C
889	---	U-C-E	U-C 875°C	U-C
860	---	U-C-E	U-C-E	U-C* 850°C
844	---	U-C-E	U-C-E	U-C-E*
	<u>Slow Heating</u>			
794	---	U-E	U-E	U-E** 810°C
832	---	U-E	U-E 845°C	U-E-C**
858	---	U-E 870°C	U-E-C	U-E-C
882	U-E 910°C	U-E-C	U-E-C	U-C**
910	U-E-C	U-E-C	U-C	U-C
942	---	U-C	U-C	U-C
963	U-C	---	---	---

*Structures shown in Fig. 2.

**Structures shown in Fig. 3.

4

roughly on this curve to a temperature of about 930° to 940°C . The controlling points in such an operation, however, are the 0.01 per cent carbon values, and this carbon content is beyond the realm of accuracy of chemical analyses. It is also interesting to note that a 0.01 per cent carbon alloy represents only 100 parts per million of carbon, and in order to produce an alloy of greater purity it would be necessary to use very pure uranium indeed.

Since many of the alloys used in determining the properties of the epsilon phase were made under conditions resulting in a carbon content of about 0.05 to 0.10 weight per cent, this particular study on the effect of carbon served to clarify many problems encountered in the investigation.

Finally, it is evident that in order for carbon to affect the epsilon equilibrium, it must be in the dissolved form, either in the uranium or epsilon phases or in both. Three 20 atomic per cent silicon alloys with varying carbon contents of 0.067, 0.133, and 0.28 weight per cent were examined microscopically to determine the form of the carbon. These alloys had been cooled to room temperature from the melt in a moderately short time and thus probably retained the carbon at a solubility limit determined by the eutectic temperature of 985°C . The 0.067 per cent alloy did not show any apparent form of carbide under the microscope but the 0.133 per cent alloy did. The latter alloy had some free carbide particles and also exhibited a carbide-rimming phenomenon on any of the oxide particles which may have been present. The rimmed oxide particles were especially apparent in the 0.28 per cent carbon alloy and it can be concluded that the carbide is soluble in the melt and subsequently precipitates about any available nuclei. The precipitation probably takes place at a high temperature at which the oxide particles are solid and U_5Si_3 dendrites have not yet started to form. The brief study outlined here sets the carbon solubility in the 20 atomic per cent silicon alloy at about 0.10 weight per cent carbon near the eutectic temperature (985°C). This solubility evidently decreases at lower temperatures as it was noted in some of the peritectoid work that the amount of carbide increased on slow cooling in the 0.133 per cent carbon alloy.

5

3. Kinetics of Epsilon Formation

3.1 Mechanism of Epsilon Formation. Epsilon has been found to form by means of a peritectoid reaction at about 930°C , and the mechanism involved is that of reaction between the uranium matrix and primary U_5Si_3 to form an intermediate rim of epsilon phase. General microscopic evidence has revealed that the initial rate of formation is fairly rapid, epsilon rims having been observed in cast alloys which were furnace cooled through the epsilon range. However, since the transformation must be completed by means of diffusion through the epsilon rim, the factors of diffusion in the solid state will control the rate of formation.

3.2 Effect of Solid Diffusion on the Rate of Formation of Epsilon. The problem involved in this particular case is the mutual exchange of silicon and uranium atoms between the reacting phases and through a constantly widening rim of epsilon. It is evident that in order for such an exchange to take place, silicon and uranium must diffuse through the epsilon rim and must be motivated by a concentration gradient, however small. In other words, the epsilon rim must have a composition range, so that the epsilon in contact with U_5Si_3 can be slightly higher in silicon than the epsilon in contact with uranium matrix. An interesting bit of conjecture in this respect can be derived from the fact that the reaction proceeds more rapidly at temperatures about 100° to 200°C below the peritectoid temperature. While a large measure of this increased rate can be attributed to the "distance from equilibrium" effect, it may be possible that the composition vertical defining the epsilon phase may be widening into a composition band at lower temperatures. Such a phenomenon would materially aid the diffusion process as has been mentioned above. Other factors influencing solid diffusion and consequently the rate of formation will follow in order.

3.3 Effect of Temperature on the Rate of Formation of Epsilon. It is common knowledge that an important factor in any reaction rate is the driving force as measured by the relative distance to equilibrium. The scale on which metallurgical equilibrium is generally plotted is temperature, and it would be expected that the rate of epsilon formation should

increase as the temperature is lowered below 930°C. However with decreasing temperature, an adverse effect is introduced in the form of slower diffusion, thus tending to decrease the rate of formation. The two effects should combine to give a maximum rate at some temperature below 930°C.

A study of the temperature effect is shown in Fig. 4 in which a measure of the rate of formation at various temperatures can be obtained by following the hardness changes. Epsilon is a softer phase than the corresponding cast structure and the difference is great enough so that hardness measurements can be used to follow any overall changes. A series of photomicrographs in Fig. 5 illustrate the annealing sequence for the alloy used over the time interval of 92 hours. This particular alloy contained some carbon, however, and these data cannot be taken as absolute values but must be used on a relative basis since the equilibrium conditions have been changed.

Relatively speaking then, the transformation goes substantially to completion in less than 20 hours and the optimum temperature seems to be between 750° and 800°C. This optimum temperature was deduced from the initial slopes of the rate curves which were almost identical for the 750° and 800°C runs. The data in general seem to support the theoretical considerations given for temperature effect in the earlier part of the text.

There is a slight discrepancy in the hardness data in that the curves of Fig. 4 do not approach the same final hardness value. The reason for this behavior is not known at present and will be known only after a more detailed study is made of the epsilon phase structure.

3.4 The Effect of Impurities on the Rate of Formation of Epsilon.

The only impurity which has been found to influence the rate of formation to any extent is carbon. The effect appears through a lowering of the equilibrium temperature and, consequently, very slow rates of formation have been found for alloys containing carbon in the 825° to 875°C region. The study of formation rate for pure epsilon alloys remains to be done.

Work on the effect of additions of various elements on a ternary basis is covered in a later section. Eleven elements were investigated,

and to date no obvious changes have been produced on the epsilon equilibrium. Whether any of the elements have any marked effect on the rate of diffusion is not known.

3.5 The Effect of Particle Size on the Rate of Formation of Epsilon.

It was noticed early in the epsilon work that small eutectic particles of U_5Si_3 could be completely converted to epsilon in a reasonable time. The particles were small enough so that they "rimmed" through and did not have to undergo the slow process of silicon diffusion through a widening phase rim. This evidence led to the belief that chill casting would serve to break down the U_5Si_3 dendrite and permit shorter annealing times. A short study was made in this respect by casting into copper, graphite, and silica-investment molds. It was found that copper gave a very fine distribution of U_5Si_3 with graphite a close second. The silica mold produced a larger dendrite size. Photomicrographs in Fig. 6 illustrate the various particle sizes obtained.

The effect of particle size can be seen from the results of Fig. 4 which show that the annealing time for complete transformation may be cut to 15 to 20 hours at $750^\circ C$ by using a chill casting made in copper.

4. Corrosion Studies

4.1 General. The corrosion resistance of epsilon has been mentioned as an outstanding property in connection with its possibilities for use where there is direct contact with cooling water. Accordingly, an extensive study was made to determine the corrosion rates of epsilon alloys under varying experimental conditions. The procedure used was that of prolonged contact in distilled water, with weighings being taken at definite intervals to determine the loss in weight. The index of corrosion was then calculated as the total loss in weight per unit area with the units of milligrams per square centimeter in all cases. To make the work comparable to previous determinations on uranium metal, base temperatures of $70^\circ C$ and $100^\circ C$ were used.

It must be borne in mind that the physical structure of an alloy will have an important bearing on its corrosion behavior, especially if the alloy is of a duplex nature with phases of varying corrosion

resistance. For example, all the cast silicon alloys have a uranium matrix susceptible to corrosion, and this matrix will determine the overall behavior of the alloys. The high silicon epsilon alloys, however, undergo a change in phase-proportion and become structures of continuous epsilon matrix which will then control the corrosion behavior. Any free uranium phase will exist in the form of segregated islands and will only effect the initial corrosion rate through surface effects. In view of these considerations, it can be seen that casting conditions will play an important role in corrosion work, for they will control the continuity of the epsilon matrix and the size of uranium islands.

The corrosion data obtained have been plotted in Fig. 7 and 8 with the former covering the 100°C tests and the latter the 70°C tests. These data summarize the results obtained in distilled water for uranium, chill-cast alloys, and "epsilonized" alloys. It can be readily seen that the two plots are basically similar, with the 70°C corrosion being much the slower. Inspection of the corrosion data shows that epsilon has a very good corrosion resistance indeed, for the 23 atomic per cent alloy actually gained a little weight over the 500 hour test period. This phenomenon was due, probably, to some sort of film formation on the surface of the particular alloy under test. The lower silicon alloys also approach a zero corrosion rate after about 100 hours and the initial loss may be attributed to the islands of free uranium phase exposed at the surface. Regarding the data on the cast alloys, corrosion proceeded quite readily and the rate seemed to increase as the test progressed. In fact, some of the alloys began to disintegrate as the matrix was progressively penetrated.

4.2 Experimental Variables. A general survey of experimental variables which might affect the corrosion data was undertaken and the results are listed.

(a) Effect of Annealing Time. In this respect it was found that a 16 hour anneal was the minimum time required to "epsilonize" samples for corrosion testing. Microscopic examination has shown that this is not always the stage of 100 per cent conversion, but evidently the corrosion resistance is not much improved by further annealing.

(b) Effect of Various Conditions of Corrosion Testing.

Type of System. Static, reflux, and continuous-flow systems were tried, but no significant differences were noted. It is probable that a continual flow of corroding medium does not influence the rate where such dilute systems are concerned.

Effect of Chloride Ion. Solutions containing 2 and 5 ppm of chloride ion were used but did not seem to alter the corrosion rate of silicon alloys within the experimental error as determined by weighing restrictions.

Effect of Gas. To test the effect of gases in solution, air, hydrogen, and oxygen were bubbled through the corroding medium for long periods of time. No significant results were observed although oxygen seemed to produce a slight weight increase in the extended test period.

Effect of Possible Film Formation. A film or coating of an oxide nature apparently forms on epsilon alloys during corrosion and serves to protect the alloy from further corrosion. Attempts have been made to remove this film by a nitric acid treatment which would then put the results on an absolute rather than a relative basis. A slow, continuous corrosion of epsilon has been found which may have been camouflaged by film effects in the ordinary distilled water test. There is still some question as to whether a relative or absolute corrosion result is desired for practical purposes.

Effect of Possible Galvanic Action. Although the test conditions used in most of the epsilon work precluded any galvanic effects, it was thought that such data might be of use at a future date in regards to a possible canning operation. A preliminary test with epsilon in contact with aluminum did not show anything significant in the way of a galvanic effect. However, in order to complete the study, a test series of ten different metals in contact with epsilon was run in boiling distilled water. Preliminary examination has failed to reveal any noticeable galvanic corrosion. The metals used were silver, aluminum, beryllium, copper, lead, zinc, tin, nickel, monel, and stainless steel.

The experimental results which were obtained on small laboratory samples of epsilon were recently confirmed by a slug corrosion test of

long duration⁽³⁾. An aluminum canned, unbonded slug of epsilon was pinholed and corroded in boiling distilled water for 94 days. The canned slug on measurement showed a diameter increase of about 2.5 to 5.0 mils caused by accumulation of corrosion products. This result may be considered very favorable compared to that obtained on a similarly tested uranium slug which gave an 80 mil diameter increase in 3 days.

4.3 High Temperature Corrosion Studies. Some brief studies have been made recently on the corrosion resistance of epsilon at higher temperatures and in different media.

(a) Corrosion in Air at Elevated Temperatures. Epsilon alloy in the higher silicon concentrations (20 to 23 atomic per cent) stands up quite well when heated in air at temperatures of 100° and 200°C. At 300°C it appears to oxidize quite readily and the activating temperature in air is evidently between 200° and 300°C. Uranium, needless to say, oxidizes very rapidly at temperatures of 100°C and over.

(b) Corrosion in Hydrogen at Elevated Temperatures. Tests have been carried out to determine the hydriding properties of epsilon alloys at temperatures of 225° and 325°C. It has been found that high epsilon alloys bear up quite well under tank hydrogen for at least 4 hours at these temperatures, whereas uranium and cast silicon alloys disintegrate into a fine powder at 225°C in 20 min.

(c) Corrosion in a Molten, Lead-Bismuth Eutectic Mixture at Elevated Temperatures. A preliminary test was made to determine the behavior of epsilon in a high-temperature medium, such as a molten, lead-bismuth eutectic mixture at 425°C. The run was made for 5 hours under vacuum, and it was found that some attack had taken place as evidenced by surface roughening and an over-all gain in weight. A further study of this type of high temperature corrosion is under way, and quantitative results will be obtained.

(d) Corrosion in a Steam Autoclave^(3,4). A sample of epsilon was corroded in a steam autoclave at 125 psi (178°C) for 52 days and the sample examined for signs of corrosive action. The results seemed to indicate that epsilon under these conditions corrodes only slightly faster than in boiling distilled water.

A controlled test was run in which aluminum canned, unbonded slugs of epsilon and uranium were pinholed and subjected to the autoclave conditions previously mentioned. The uranium slug showed a characteristic failure after 2 hours while the epsilon test continued for 16 days without any noticeable changes. After another 31 days of continuous testing, the canned slug evidenced some localized swelling, especially at the ends. On removing the aluminum can, it was found that the epsilon slug had not corroded perceptibly, but had cracked badly during the test. Microscopic examination revealed that the epsilon phase had withstood the corrosive action of the steam very well. A number of small isolated areas of some non-metallic phase were evident in the specimen and these may well have been original uranium areas. Such a uranium phase attack could have led to changes in volume which accounted for the corrosion cracking. This particular test was performed on epsilon material made at an early date and the results should be regarded as only tentative. The epsilon phase in itself seems to possess adequate steam corrosion resistance properties.

5. Physical Properties

All the results obtained and listed below are for alloys containing 0.05 to 0.10 weight per cent carbon.

5.1 Density. The densities of cast silicon and epsilon alloys were determined over a silicon range of 15 to 25 atomic per cent and the data are plotted in Fig. 9. As expected, the cast alloy curve is continuous in this silicon range since the microstructures involved contain continuously varying relative amounts of uranium and U_5Si_3 . The curve for epsilon alloy, however, shows a break at the epsilon phase composition, at which point the density of epsilon can be evaluated at approximately 15.45 g/cm^3 .

It should be expected that on annealing a cast silicon alloy to the corresponding epsilonized state, a change in density should occur which would be a function of the silicon content with a maximum at the epsilon composition. The curve relationships bear this point out, and, if the density changes on the percentage basis are plotted against the corresponding silicon contents, the curve shown in Fig. 11 is obtained.

This shows the predicted maximum at the epsilon composition. Such a density function could only be derived from a change in phase relationships.

5.2 Hardness. The hardness data were taken from the same alloy series as was used in the density work and the corresponding plots are shown in Fig. 10. Evidently epsilon is a softer phase than either U_5Si_3 or the epsilon structures below 23 atomic per cent silicon. Since the same considerations that were derived for the changes in density should apply for changes in hardness, the curve in Fig. 11 is obtained, which now shows a minimum at the epsilon composition.

5.3 Compressive Strength. Stress-strain curves in compression are shown for epsilon alloys in Fig. 12. The yield point in compression seems to be at about 125,000 psi and is apparent after a 0.5 to 1 per cent reduction in length. The ultimate strength lies roughly at about 275,000 psi and the total reduction in length prior to breaking is between 12 and 16 per cent. A rough correlation with silicon content reveals that the lower silicon alloy has the highest yield point and greatest over-all plasticity.

Cast alloys have a high yield point but are very brittle and fail with very little deformation.

5.4 Tensile Strength. Some difficulty has been experienced in preparing tensile specimens from the epsilon alloy, and the main trouble has been in the casting operation. Small blowholes and porosity areas at the center of the tensile stock have interfered with the preparation of good tensile specimens. The one result which has been obtained is shown in Fig. 14, and the test shows a breaking stress of 37,000 psi at 0.25 per cent elongation. The specimen failed here, however, due to casting defects and reliable tensile data can be obtained only after the casting technique is improved.

5.5 Hot Compression. The hot compression data, shown in Fig. 13, were obtained at the Chicago laboratory⁽⁶⁾. It can be seen that both the yield point and strength curves rapidly decrease from 600° to 850°C with an apparent dip at about 750°C. This phenomenon may be due to a uranium phase change, but this has not been established. The low values

of compressive strength in the 750° to 850°C range indicate a fair amount of ductility for epsilon alloy at these temperatures.

5.6 Thermal Conductivity. The thermal conductivity of epsilon alloy was also determined at the Chicago laboratory⁽⁷⁾ and is shown in Fig. 15. The conductivity appears to be about 70 per cent of that determined recently for rolled alpha uranium, and it seems that the silicon content has a slight lowering effect.

5.7 Summary of Physical Properties. The physical properties of epsilon which have been determined to date are summarized in Table 2.

TABLE 2
PHYSICAL PROPERTIES OF EPSILON ALLOYS
CONTAINING 23 ATOMIC PER CENT SILICON AND 0.05 TO 0.10
WEIGHT PER CENT CARBON

Density	15.45 ± 0.05 g/cm ³
Hardness	28 ± 1 Rockwell "C"
Compression	
Yield Strength	
At 25°C	115,000 psi
" 600°C	55,000 psi
" 700°C	18,000 psi
" 750°C	10,000 psi
" 850°C	4,000 psi
Ultimate Strength*	280,000 psi
Reduction*	14.0 per cent
Tension	
Yield Strength*	37,000 psi
Ultimate Strength*	37,000 psi
Thermal Conductivity	
At 25°C	0.036 cal/(sec cm ² °C/cm)
" 50°C	0.041 cal/(sec cm ² °C/cm)
*At 25°C	

6. Fabricating Properties of Epsilon

6.1 Casting Properties. The castability of epsilon alloys has not been investigated to any great extent, and the facts that are known on this subject have been obtained mainly through observations on the melting practice used to date. The primary consideration is temperature and on examining the uranium-silicon equilibrium diagram, it can be seen that castability is essentially a high temperature problem. At 23 atomic per cent silicon, the liquidus is at approximately 1500°C, and its slope is such that small shifts in the silicon composition will have an important bearing on the metal fluidity. Because of particle size considerations, most of the work which has been done has been on chill casting into copper and graphite molds, and this practice has introduced some porosity at the center of the ingots. This problem of porosity has influenced the making of tensile specimens from ingot material and will require further investigation.

Regarding fluidity, it has been found that melts cast from 1750°C into bottom-poured graphite molds are fluid enough to give a metal rise in the mold of at least 12 in. This rise is a function of the diameter of the rise channel and the lower limit for free flow seems to be about 5/8 in.

Lastly, there are the refractory problems which have been encountered. Beryllia-lined graphite crucibles and stopper rods have been used successfully, but have introduced the problem of carbon pick-up, if and when the lining failed. The use of such graphite crucibles seems to be entirely feasible for large scale melting since the carbon pick-up (0.05 to 0.1 per cent) has not yet been shown to have an adverse effect on the properties of epsilon. Attempts to produce carbon-free alloys have necessitated the use of beryllia crucibles and stopper rods which have proved highly satisfactory in the few melts which have been made.

6.2 Extruding Properties. The first attempts at hot extrusion of epsilon billets did not prove very successful. The product was quite ragged, and the characteristic "christmas tree" effect was evident. Later attempts showed some signs of promise, but only after the following problems were recognized.

(a) Lubrication. It was evident that some sort of die lubrication was necessary and this was provided by incasing the billets in copper tubing. Quite an improvement was noticed and evidently resulted from the lubricating effect of the copper. However, the ends of the billets were unprotected in this particular test and led to some undesirable secondary effects which will be mentioned later. The end of the billet entering the extrusion die may well receive a better start if it is also lubricated with copper, and plans are now under way in which the ends of the copper-jacketed billets will be spun closed for complete protection.

(b) Oxidation. The extrusion set-up has not provided for very complete protection of the material as it is being heated to the extrusion temperature (750° to 800°C). In fact, it is believed that the effects of surface oxidation, which are necessarily exothermic, have actually served to raise the temperature of the charge to a higher level than can be allowed by theoretical considerations. It is hoped that the spinning operation mentioned in (a) above will provide the protection needed in this operation.

(c) Temperature Control. The extrusion temperature has been generally kept at about 750° to 800°C , but the degree of accuracy involved is not known. Effects of surface oxidation have been mentioned as serving to raise the billet temperature appreciably, and this may make the control operation all the more difficult. The need for temperature control arises from the fact that alloys containing carbon (0.05 to 0.10 weight per cent) have been used in all the work, and it has been shown conclusively that carbon has a marked lowering effect on the transformation temperature. If the structure of the alloy is such that decomposition starts in the range 800° to 850°C , then it can be easily seen why temperature control is such an important variable. Some microscopic evidence in this respect has been gathered in recent extrusion studies. Samples of alloys which were heated but not extruded, and also of extruded alloys, have shown that the epsilon structure has "reverted" back to a finely-divided mixture of uranium phase and U_5Si_3 . It is evident, then, that the extrusion temperature attained was above the epsilon decomposition point for the alloys under test.

Present extrusion work is proceeding with due recognition of the importance of lubrication, oxidation effects, and temperature control as determining factors of the operation.

6.3 Machining Properties. Epsilon alloys can be machined under the proper conditions although they are considerably more difficult to handle than uranium metal. Tensile specimens complete with threads have been made, and not too much trouble has been encountered in machining various cylindrical shapes for sundry physical and corrosion testing. The effect of carbon on the machining properties is unknown, and the elimination of this impurity may serve to better the machining qualities.

7. Surface "Epsilonizing"

Surface "epsilonizing" has been tried recently in the hopes of producing a material with a much lower over-all silicon content. The preliminary tests attempted were a "pack-siliconizing" treatment in which uranium specimens were packed in powdered silicon, Si, or carborundum, SiC, powders and heated in vacuum at 900°C. The carborundum test did not show any unusual results, but the silicon pack produced what appears to be one of the uranium compounds high in silicon. The test was of rather long duration (20 hours) and all of the uranium reacted with the excess of silicon to go into combination. Preliminary tests look quite promising and a study program is now underway which should yield some interesting results.

8. Uranium-Silicon Ternary Studies

An investigation has been started on a series of uranium-silicon ternary systems in order to evaluate possible alloying effects on the epsilon reaction and on the corrosion resistance. The procedure followed was that of making up ternary mixtures containing about 15 atomic per cent silicon and from 1 to 10 atomic per cent of the alloying component. Samples of the ternary alloys were subsequently "epsilonized", examined microscopically, and then subjected to corrosion testing in boiling distilled water.

The elements studied included columbium, nickel, iron, beryllium, aluminum, zirconium, and copper with molybdenum, tin, titanium, and germanium now under test (June, 1945).

It was found that the epsilon reaction proceeded normally in all the ternaries studied with the possible exception of the zirconium system. No large shift in the epsilon composition was apparent, and the speed of the reaction did not seem to be markedly affected. Copper and iron may have served to increase the rate of formation, but this was not definite. It seems that a majority of the alloying elements form binary compounds with uranium. Columbium and zirconium are the exceptions, and these appear to combine with silicon to form binary compounds, thus lowering the effective silicon content. Some of the elements may have a limited solubility in the uranium phase but this is difficult to determine under the microscope from these preliminary studies.

The aluminum ternary has shown some corrosion-resistant properties in the as-cast state without "epsilonizing" and the system is under more detailed investigation.

9. Summary

- (1) The epsilon phase of the uranium-silicon binary system has been found to form by means of a peritectoid reaction at about 930°C .
- (2) The epsilon-peritectoid equilibrium is markedly affected by small amounts of carbon which tend to lower the peritectoid temperature.
- (3) Other elements do not seem to influence the equilibrium to any great degree.
- (4) The epsilon phase has been found to possess very good corrosion resistance in boiling distilled water and indications are that it also has good resistance to air, hydrogen, and steam at elevated temperatures.
- (5) The physical properties of epsilon as determined to date indicate a fair amount of ductility. Improvements in casting and handling techniques will serve to give a better evaluation of these properties.
- (6) Surface "siliconizing" has been shown to be possible and a study of practical applications is under way.

Figure 1. The effect of carbon on epsilon peritectoid.
Silicon held constant at 20 atomic per cent.

a. 500X

a: Alloy quenched from 956°C;
white U_5Si_3 in dark U matrix;
some oxide particles showing.

b. 500X

b: Alloy quenched from 860°C;
 U_5Si_3 and U.

c. 500X

c: Alloy quenched from 844°C;
epsilon starting to form as
"rims" on some U_5Si_3 dendrites.

Figure 2. Epsilon "rim" formation on slow-cooling: photomicrographs establishing temperature of epsilon formation by slow-cooling technique. Alloy (PE-2) contains 20.5 atomic per cent Si and 0.133 weight per cent C (electrolytically etched and heat-tinted).

a. 500X

a: Alloy quenched from 794°C;
epsilon, dark U, and some
oxide particles.

b. 500X

b: Alloy quenched from 832°C;
epsilon starting to decom-
pose with U_5Si_3 particles
appearing.

c. 500X

c: Alloy quenched from 882°C;
epsilon completely decom-
posed into U and U_5Si_3 .

Figure 3. Photomicrographs establishing temperature of epsilon decomposition by slow-heating technique. Alloy (PE-2) contains 20.5 atomic per cent Si and 0.133 weight per cent C (electrolytically etched and heat-tinted).

Figure 4. Effect of temperature on the rate of formation of epsilon. Chill-cast alloy, E-11; 20.5 atomic per cent Si, 9.05 to 0.10 weight per cent C.

a. 250X

a: Annealed 8 hours at 750°C;
U₅Si₃ centers in speckled
epsilon with some excess
U (black). Reaction about
50 to 75 per cent complete.

b. 250X

b: Annealed 16 hours at 750°C;
microconstituents as of a
reaction about 95 per cent
complete.

c. 250X

c: Annealed 92 hours at 750°C;
reaction 100 per cent com-
plete.

Figure 5. Epsilon formation: photomicrographs of alloy annealed at 750°C for specified times. Alloy contains 20.5 atomic per cent Si and 0.05 to 0.10 weight per cent C (electrolytically etched and heat-tinted).

a. 100X

a: Cast into copper mold;
half-inch round.

b. 100X

b: Cast into graphite mold;
half-inch square.

c. 100X

c: Cast into silica-invest-
ment mold; quarter-inch
round.

Figure 6. Particle size obtained on casting U-Si alloy in the range of 20 to 23 atomic per cent Si. U_2Si_3 in dark matrix of U (electrolytically etched and heat-tinted).

DECLASSIFIED

24

Figure 7. Corrosion of epsilon alloys in distilled water at 100°C. Numbers on the curves give the silicon content in atomic per cent.

Figure 8. Corrosion of epsilon alloys in distilled water at 70°C. Numbers on the curves give the silicon content in atomic per cent.

Figure 9. Density of epsilon alloys ("epsilonized" at 750°C). Carbon content, 0.05 to 0.10 weight per cent.

Figure 10. Hardness of epsilon alloys ("epsilonized" at 750°C). Carbon content, 0.05 to 0.10 weight per cent.

Figure 11. Changes in density and hardness resulting from "epsilonising" cast silicon alloys at 750°C. Carbon content, 0.05 to 0.10 weight per cent.

RECEIVED

Figure 12. Stress-strain curves (in compression) of epsilon alloys. Numbers on the curves give the silicon content in atomic per cent. Carbon content, 0.05 to 0.10 weight per cent.

Figure 13. Hot compression of epsilon alloy containing 23 atomic per cent silicon. Carbon content, 0.05 to 0.10 weight per cent.

Figure 14. Stress-strain curve (in tension) of epsilon alloy containing 23 atomic per cent silicon. Carbon content, 0.05 to 0.10 weight per cent.

Figure 15. Thermal conductivity of epsilon alloys. Numbers on the curves give the silicon content in atomic per cent. Carbon content, 0.05 to 0.10 weight per cent.

30000000

~~CONFIDENTIAL~~

-31-

REFERENCES

- (1) Cooper, C. M., MUC-CMC-322, Nov. 24, 1944.
- (2) Cullity, B., MPR, Vol. 12 B, No. 6.7 (1945).
- (3) Brugmann, E. W., MUC-EWB-385, June 9, 1945.
- (4) Brugmann, E. W., CT-2743, p. 61, February, 1945.
- (5) Brugmann, E. W., CT-2794, p. 83-88, March, 1945.
- (6) Foote, F., CT-2794, p. 24, March, 1945.
- (7) Foote, F., CT-2668, p. 23, January, 1945.

CONFIDENTIAL

~~CONFIDENTIAL~~