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SYNTHESIS AND FABRICATION OF REFRACTORY URANIUM COMPOUNDS

Summary Report — May 1959 Through December 1960

By
K. M. Taylor
C. H. McMurtry

February 1961

Research and Development Division
Carborundum Company
Niagara Falls, New York

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Contract No. AT-(40-1)-2558

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FOREWORD

The work described in this report was done for the United States Atomic Energy Commission by The Carborundum Company under Contract No. AT (40-1)-2558. It is a part of the AEC Fuel Cycle Development Program, and covers the period of May, 1959 through December, 1960.

In addition to the authors, the following persons contributed to the work described in this report: C. A. Lenie, P. A. Smudski, P. E. Doherty, L. N. Hailey, and T. J. Keaty.

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I. INTRODUCTION

The object of this investigation was to develop refractory uranium materials possessing sufficient advantage over uranium dioxide to warrant their use as reactor fuels.

Numerous properties, in addition to refractoriness, affect the suitability of a material for fuels. However, uranium density and thermal conductivity are highly important considerations. It was, therefore, decided to center attention on uranium monocarbide, uranium mononitride and the silicide, U_3Si_2, all of which have higher uranium densities than UO_2. Also, it seemed probable that the thermal conductivity of these three materials would be superior to that of UO_2 which is a poor conductor.

The work program was divided into three phases: (1) the development of methods for synthesis of the compounds, (2) fabrication of the synthesized materials into bodies suitable for testing, and (3) the determination of such properties as thermal conductivity, thermal expansion, and high temperature strength.

The development of economical methods, both for synthesis of the compounds and fabrication of the bodies, has been emphasized, since the ultimate aim of the fuel cycle program is to decrease the cost of power from nuclear reactors.

II. SYNTHESIS EXPERIMENTS

A. Uranium Monocarbide

Three approaches were considered for the preparation of UC: (1) reduction of an oxide (UO_2 or U_3O_8) by carbon, (2) reaction of ammonium diuranate and carbon, and (3) the direct combination of uranium metal and carbon.

1. Reaction of Uranium Oxide and Carbon

Carbon was heated with both UO_2 and U_3O_8 to produce UC according to the following reactions:

$$UO_2 + 3C \longrightarrow UC + 2CO$$

$$U_3O_8 + 11C \longrightarrow 3UC + 8CO$$

The oxide was Mallinckrodt's minus 200 mesh ceramic powder (natural uranium). The carbon was R. T. Vanderbilt Company's Thermax Thermatomic Carbon, produced by the thermal decomposition of methane. It had an ash content of 0.05 percent and a particle size of less than 2 microns.

The reaction mixture was usually prepared for furnacing as follows: the oxide and carbon were mixed by dry ball-milling for 24 hours in a rubber-lined mill with stainless steel balls and then pressed into pellets, 5/8 inches by 5/8 inches, at 15,000 - 20,000 pounds per square inch, using about 2 percent of water as a temporary binder.

A few experiments indicated the possibility of omitting the pelletizing step by simply heating the mixed powders. This has the advantages of saving pelletizing time and producing a softer clinker which is more readily crushed to a powder. However, it appears more difficult to obtain a complete reaction if pelletizing is omitted, probably because the particles of UO_2 and carbon are in less intimate contact. Chemical analysis of a representative 1500 gram batch of UC prepared from a non-pelletized mix was as follows:

	%
Uranium	94.58
Combined Carbon	4.58
Uncombined Carbon	0.49
Nitrogen	trace
Iron	trace
Oxygen	0.50

In the above experiment, the mix was heated for 8 hours in a vacuum at 1750°C. Both uncombined carbon and oxygen are abnormally high, indicating incomplete reaction, which is confirmed by x-ray analysis.

Three types of furnaces were tried for heating the reaction mixture: (1) induction furnace with flowing argon atmosphere (Figure 1); (2) alumina muffle tube furnace with flowing argon atmosphere (Figures 2 and 3); and (3) vacuum induction furnace. A sketch and photograph of the vacuum induction furnace are shown in Figures 4 and 5, respectively. The vacuum pump was a four-stage mechanical booster pump, Model KMB-30, purchased from Kinney Manufacturing Company, and has a capacity of 30 cubic feet per minute. A vacuum of 5 to 10 microns was

obtained at room temperature and about 50 microns at 1700-1800°C. after the reaction had been completed; during the reaction the pressure depended upon the rate of heating and size of the mix.

In most cases, graphite crucibles were used to contain the reaction mix, although tantalum crucibles were used in a few experiments. The latter appear to be satisfactory but unnecessary.

In regard to the results obtained with the different furnaces, there appear to be no basic reasons why almost any type of furnace cannot be used satisfactorily so long as the proper temperature and atmospheric conditions can be maintained. However, the results were somewhat erratic with the particular induction furnace used in these experiments, probably because it was difficult to exclude air completely from the reaction chamber. Good results were obtained in both the muffle tube furnace with flowing argon and in the vacuum induction furnace. However, the vacuum furnace is preferred because otherwise considerable quantities of expensive inert gases (argon or helium) must be used to carry off the carbon monoxide formed; if carbon monoxide is not removed, the reaction fails to go to completion.

Uranium dioxide and carbon were found to react slowly at 1400°C. Thus, when a mixture of UO_2 and carbon was heated for 4 hours at 1400°C. in a muffle furnace in flowing argon, the product, as determined by x-ray analysis, was principally UO_2 with small amounts of UC and UC_2. The preferred temperature for forming UC was found to be 1700-1800°C. The x-ray pattern of the product normally obtained by heating in this temperature range was: major phase, UC; faint indications of UO_2 and UC_2; occasional batches contained no trace of UC_2. When the furnacing temperature was higher, there tended to be larger amounts of UC_2 in the product.

It seemed possible to synthesize good quality UC by the carbon reduction of either UO_2 or U_3O_8. However, the results were more consistent with UO_2; in particular, there tended to be less UC_2 in the product when UO_2 was the starting material. This is probably explained by the fact that U_3O_8 is partially reduced thermally to UO_2; therefore, the calculated amount of carbon to react with U_3O_8 according to the equation

$$U_3O_8 + 11C \longrightarrow 3UC + 8CO$$

may be excessive, depending upon the exact furnacing conditions such as rate of temperature rise. Thus, in some instances, the product

of the foregoing reaction contained 6 to 7 percent carbon as contrasted to the theoretical of 4.80 percent for pure UC.

Many batches of UC have been made by heating stoichiometric mixtures of UO_2 and carbon in the vacuum induction furnace at 1750-1800°C. The size of the batches varied from about 30 grams to 6 pounds. The range in chemical analysis of the product was as follows:

	%
Uranium	94.50 - 95.40
Carbon	4.65 - 4.90
*Oxygen	.05 - 0.35
Nitrogen	trace - 0.10
Iron	trace - 0.10

*Determined by vacuum fusion.

X-ray analysis usually, but not always, indicated trace amounts of UO_2 and UC_2 in addition to the major phase of UC.

2. Reaction of Ammonium Diuranate and Carbon

According to Katz and Rabinowitch[1], ammonium diuranate decomposes on heating as follows:

$$9(NH_4)_2U_2O_7 \longrightarrow 2N_2 + 14NH_3 + 6U_3O_8 + 15H_2O$$

If it is assumed that the U_3O_8 formed reacts with carbon according to the equation

$$U_3O_8 + 11C \longrightarrow 3UC + 8CO$$

then, theoretically, 12.36 percent carbon is needed in the reaction mixture of ammonium diuranate and carbon. However, a consideration of the factors involved indicates that the reaction may not proceed as outlined above. For example, U_3O_8 may thermally decompose, at least in part, to UO_2 before reduction by carbon takes place. Also, hydrogen formed by decomposition of ammonia, and the presence of water vapor at certain stages in the synthesis, may influence the amount of carbon required. That some such side reactions do occur is indicated by the experiments described below.

The ammonium diuranate (Mallinckrodt's minus 200 mesh) and carbon were mixed by ball-milling for several hours in a rubber-lined mill with stainless steel balls. Pellets were pressed at 15,000-20,000 pounds per square inch and reacted in alumina boats under various conditions.

The first experiment was based on the assumption that ammonium diuranate would decompose to U_3O_8 under the reaction conditions and the carbon would then react with the U_3O_8 to form uranium carbide. The pellets were heated in a ceramic tube furnace in an argon atmosphere. A temperature of about 700°C. was reached in approximately 20 minutes and the maximum temperature of 1700°C. in about 3 to 4 hours. The pellets were held at 1700°C. for one hour and then allowed to cool, in argon, to room temperature. The results for x-ray and chemical analyses are shown in Experiment 1, Table No. I.

These results indicated that a large amount of uranium dicarbide was formed. The stoichiometric amount of carbon for UC is 4.80 percent. Additional experiments were undertaken as indicated above except that smaller amounts, 11.90 and 10.00 percent of carbon, were used in the reaction mixture. The results for x-ray and chemical analyses are shown in Table No. I, Experiments 2 and 3, respectively.

These results indicate that 11.90 percent carbon is too high and 10.00 percent is somewhat low for stoichiometric UC. The results also suggest the possibility that the reaction did not take place between carbon and U_3O_8 but rather carbon and another oxide. It was now assumed that the final decomposition product of ammonium diuranate under the reaction conditions was UO_2. Under this assumption, 10.34 percent carbon would be needed and additional experiments were made on this basis. The final composition of the product was very sensitive to the reaction conditions as shown in Table No. II.

The results of these experiments indicate the possibility of preparing stoichiometric uranium monocarbide by this process but considerable additional study will be required.

3. Reaction of Uranium and Carbon

This method of preparation was used exclusively in connection with a simultaneous synthesis and fabrication process which will be described under fabrication of uranium carbide.

TABLE NO. I

Products Obtained by Reacting Carbon with Ammonium Diuranate

Experiment No.	Amount of Carbon, %	X-Ray Analyses	Chemical Analyses, %	
1	12.36	Strong UC Moderate UC_2 Indication UO_2	Uranium Total Carbon Nitrogen Iron	92.59 7.22 < 0.10 0.01
2	11.90	Moderate UC Weak to Moderate UC_2	Uranium Total Carbon Nitrogen Iron	92.65 6.53 < 0.10 0.13
3	10.00	Strong UC Faint UO_2 Indication UC_2	Uranium Total Carbon Nitrogen Iron	94.53 4.16 < 0.10 0.003

TABLE NO. II

Effect of Heating Conditions on the Reaction Product of Carbon and Ammonium Diuranate

	Experiment 1	Experiment 2	Experiment 3
Atmosphere	Vacuum	Argon	Argon
Time to Reach 700°C, min.	40	40	40
Time to Reach 1700°C, hr.	1	2	4
Holding Time, hr.	1	1	1
Total Carbon, %	3.88	4.15	5.51
X-Ray Analysis			
UC	Major	Major	Major
UC_2	Weak	Weak	Moderate to Strong
UO_2	Faint	Faint	Faint

B. Synthesis of Uranium Mononitride

A review of the literature (see appendix) indicated that of the uranium nitrides, only the mononitride, UN, is stable in a vacuum above 1300-1400°C. The most successful preparation methods for UN disclosed in the literature were: (1) the reaction of UH_3 with nitrogen or ammonia, and (2) the reaction of UCl_4 with ammonia. After some consideration of possible costs of several potential processes, it was decided to investigate the following:

a. The reaction of uranium oxide, carbon and nitrogen.

b. The reaction of uranium metal (or hydride) and nitrogen.

c. The reaction of ammonium diuranate, carbon and nitrogen.

1. Reaction of Uranium Oxide, Carbon and Nitrogen

Uranium oxide was investigated as a starting material for producing uranium nitride because this method appeared attractive economically. The desired reactions are illustrated by the following equations:

$$2UO_2 + 4C + N_2 \longrightarrow 2UN + 4CO$$

$$2U_3O_8 + 16C + 3N_2 \longrightarrow 6UN + 16CO$$

A study of the literature indicated that the probability for these reactions is good, since UC is unstable in nitrogen above 1100°C., while UN is stable in nitrogen up to considerably higher temperatures. A possible disadvantage of this approach is that UC and UN are isomorphous, making identification of the reaction products by x-ray techniques difficult.

The first experiments were carried out as follows: Stoichiometric mixtures of UO_2 or U_3O_8 (minus 200 mesh) and carbon (minus 2 microns) were mixed by ball-milling for 2 hours in a rubber-lined mill with stainless steel balls. The mixtures were placed in graphite crucibles and heated at 1400 to 1850°C. in a flowing nitrogen atmosphere supplied from commercial tank nitrogen. The reaction products were also allowed to cool in a nitrogen atmosphere. Two types of furnaces were used depending upon the temperature: at 1400 to 1500°C., a ceramic tube muffle furnace was used with holding

times up to 48 hours; at 1550 to 1850°C., an induction furnace (Figure 1) was employed with holding times up to several hours.

At the lower temperatures (1400-1500°C.) the rate of reaction was so slow that the reaction did not go to completion during the period at which the maximum temperature was maintained. The product consisted of a mixture of U_2N_3, UO_2 and uncombined carbon; however, carbide impurities were apparently not formed. (See Experiment 1, Table No. III). At the higher temperatures (1750-1850°C.) in the induction furnace, the reaction rate was greater, but there was a tendency to form carbides and solid solutions of nitrides and carbides. The products were also characterized by some oxidation believed to have been caused by poor atmosphere control during furnacing (as an example, see Experiment 2, Table No. III). Therefore, additional experiments were carried out using the special alumina tube muffle furnace, illustrated in Figures 2 and 3, where both high temperature and more positive atmosphere control were possible. In addition, several other changes in procedure were made: the milled mix was pelletized into 0.5 by 0.5 inch cylinders by pressing at 15,000-20,000 pounds per square inch with about two percent water as a temporary binder; the pelletized mix was heated on an aluminum nitride plate instead of in a graphite crucible; the commercial nitrogen was purified by passing it through activated alumina to remove possible moisture and then through heated copper turning to remove oxygen (in one or two experiments Matheson's purified nitrogen was substituted for laboratory purified nitrogen); in some experiments, the uranium oxide-carbon mix was prepared by ball-milling for 24 hours instead of two hours; and finally, in the majority of the experiments, the reaction product was cooled in an inert atmosphere instead of in nitrogen. This last modification was found necessary because the product desired was UN, and although UN may have been produced at the nitriding temperatures of 1700 to 1750°C., it converted, at least partially, to the higher nitrides when cooled slowly in nitrogen.

Table No. III summarizes some representative experiments on the preparation of UN by nitriding stoichiometric mixtures of the oxide and carbon. Comments have already been made on Experiments 1 and 2. Experiments 3 and 4 were designed to compare UO_2 and U_3O_8 as starting materials. Since the product was cooled in nitrogen in both cases, the major product was U_2N_3. However, the free carbon content of the product was much higher when U_3O_8 was used. This is probably because there was not a direct reaction between

TABLE NO. III

Representative Experiments on the Synthesis of UN by Nitriding Mixtures of Uranium Oxide (UO_2 or U_3O_8) and Carbon

Experiment No.	Oxide	Container Material	Furnace Type	Atmosphere	Reaction Temperature, °C.	Reaction Time, hr.	Analyses of Product X-Ray		Chemical, %	
1	U_3O_8	Graphite	Ceramic tube	Ammonia	1500	24	Major Weak Weak	U_2N_3 UO_2 Graph.	N Free C Comb. C	7.49 1.00 Nil
2	UO_2	Graphite	Induction	Nitrogen	1750	3	Major Mod. Weak	U(C, N)* U_2N_3 UO_2	U N Free C Comb. C	93.39 5.23 0.23 0.26
3	UO_2	Aluminum Nitride	Special Ceramic tube	Nitrogen	1700	4	Major Indication	U_2N_3 UO_2	U N Free C Comb. C	90.85 7.67 0.10 0.06
4	U_3O_8	Aluminum Nitride	Special Ceramic tube	Nitrogen	1700	4	Major	U_2N_3	U N Free C Comb. C	88.56 8.24 1.64 0.06
5	UO_2	Aluminum Nitride	Special Ceramic tube	Nitrogen Argon Cooled in argon	1600 1600	3 3	Major Weak	U_2N_3 UO_2	U N Free C Comb. C	93.20 4.70 0.05 0.23

TABLE NO. III (cont'd)

Experiment No.	Oxide	Container Material	Furnace Type	Atmosphere	Reaction Temperature, °C.	Reaction Time, hr.	Analyses of Product X-Ray		Chemical, %	
6	UO_2	Aluminum Nitride	Special Ceramic tube	Nitrogen Argon Cooled in argon	1700 1700	3 1	Major Mod. Weak	UN U_2N_3 UO_2	U N Tot. C	93.81 5.06 0.17
7	UO_2	Aluminum Nitride	Special Ceramic tube	Nitrogen Argon Cooled in argon	1700 1700	1 3	Major Weak Faint type	UN UO_2 UC_2	U N Free C Comb. C	93.84 5.02 0.04 0.11
8	UO_2	Aluminum Nitride	Special Ceramic tube	Nitrogen Argon Cooled in argon	1700 1700	3 3	Major Very faint	UN UO_2	U N Free C Comb. C	94.41 5.20 0.04 0.07

*Solid solutions of uranium carbide and uranium nitride.

the U_3O_8 and carbon under the experimental conditions, but rather considerable thermal decomposition of U_3O_8 to UO_2 and then reaction between UO_2 and carbon. In the remainder of the experiments shown in Table No. III, the product of nitriding was held at the maximum temperature for a period of 1 to 3 hours in an inert atmosphere and then cooled in an inert atmosphere in order to obtain the mononitride. The best results were obtained under the conditions of Experiment 8. The mononitride could also be obtained, of course, by decomposing the higher nitrides in vacuum.

It seems probable that the nitrogen analyses reported in Table No. III are somewhat low. Recent analyses by the National Research Corporation of the same samples, show nitrogen contents about 0.4 - 0.5 percent higher than those obtained by Carborundum. Uranium nitride, in the form of fine powder, is pyrophoric and must be handled with great care to prevent loss of nitrogen by oxidation. This is a possible source of error in the determination of nitrogen.

2. Reaction of Uranium and Nitrogen

The work described in the preceding section demonstrated that a good grade of UN can be made by nitriding a stoichiometric mixture of UO_2 and carbon. As a basis of comparison, experiments were also conducted on nitriding uranium metal. In nearly all instances, 100 to 250 mesh natural uranium metal shot, obtained from National Lead Company, was used. The following impurities were found in the metal powder as received:

	%
Oxygen	0.10
Total Carbon	0.08
Iron	0.07
Nitrogen	0.03

The metal was treated with dilute nitric acid, followed by washing with distilled water and acetone, to remove oxide film before being used to make UN.

Several procedures were tried for converting the uranium metal shot to UN, as illustrated by the following experiments:

Experiment 1. The cleaned metal shot was placed in an alumina boat and heated in a ceramic tube furnace in laboratory purified nitrogen at 800°C. for 8 hours. The nitrided product was then transferred to a graphite crucible and heated in a vacuum induction furnace (Figure 4), for one hour at 1600°C. to decompose the higher nitrides to UN. As can be seen from Experiment 1, Table No. IV, the product picked up considerable carbon from the graphite crucible and was also contaminated with UO_2. Oxygen contamination in this case was probably caused by insufficient care in handling the nitride powder.

Experiments 2 and 3. The metal was nitrided as above except the alumina boat was replaced with one of aluminum nitride. The decomposition to the mononitride was carried out in the ceramic tube furnace by raising the temperature of the furnace to 1450°C. and holding for 8 hours in an argon atmosphere. The product (Experiment 2, Table No. IV) was principally UN with only small amounts of carbon and UO_2. Experiment 3 was a duplicate of Experiment 2, except in Experiment 3, prepurified nitrogen, obtained from the Matheson Company, was substituted for the laboratory purified nitrogen. The products of the two experiments were essentially the same, x-ray examination showing a major phase of UN with faint patterns for UO_2. It is believed that the source of oxygen here was the tank argon used in the decomposition and cooling steps.

Experiment 4. The metal was first converted to the hydride by heating in hydrogen for one hour at 250°C. The hydride was then nitrided as in Experiments 2 and 3, Table No. IV. After nitriding, the product was transferred to a tantalum-lined graphite crucible and decomposed to the mononitride by heating in the vacuum furnace at 1400°C. X-ray examination of the UN did not reveal UO_2 as in the previous experiments, thus further indicating that the source of oxygen in Experiments 2 and 3 had been the commercial argon used in the ceramic tube furnace during decomposition of the higher nitrides and cooling of the furnace. Chemical analysis confirmed the low oxygen content of the product in Experiment 4.

Since the procedure used in Experiment 4 appeared to result in a good product, a larger furnace (Figure 6) was constructed for hydriding and nitriding uranium metal shot.

The muffle was an Inconel tube, 3 inches inside diameter by 48 inches long. Stainless steel boats, holding about 1000 grams of

TABLE NO. IV

Representative Experiments on the Preparation of UN from Uranium (100-250 Mesh U shot was Nitrided in Experiments 1, 2 and 3; UH_3 was Nitrided in Experiment 4)

Experiment No.	Nitriding Conditions			Conditions for Reduction of Higher Nitrides to UN				X-Ray Analyses		Chemical Analyses, %	
	Temp. °C.	Time hr.	Container Material	Temp. °C.	Time hr.	Atmosphere	Container Material				
1	800	8	Al_2O_3	1600	1	Vacuum	Graphite	Major Weak	U(C, N) UO_2	U N Free C Comb. C Fe	94.43 4.21 0.07 0.60 0.01
2	800	4	AlN	1450	8	Argon	AlN	Major Faint	UN UO_2	U N Total C Fe	94.20 5.26 0.10 0.08
3	800	4	AlN	1450	8	Argon	AlN	Major Faint	UN UO_2	U N Total C Fe	94.48 5.24 0.04 0.09
4	250-800	6	Tantalum	1400	1	Vacuum	Tantalum	Single Phase	UN	N O	5.11 0.01

Note: Matheson's prepurified nitrogen was used in Experiment 3 while laboratory-purified nitrogen was used in Experiments 1, 2 and 4. Oxygen in Experiment 4 was determined by vacuum fusion.

nitride, were used as containers. After nitriding and cooling, the stainless steel boat was pushed into a flexible rubber tube attached to one end of the muffle and the rubber tube closed off from the Inconel tube by clamps. The closed rubber tube containing the nitride was then transferred to a glove box where the product was placed in a tantalum-lined graphite crucible preparatory to heating in the vacuum furnace.

The product obtained by the above procedure was single phase uranium mononitride, as determined by x-ray analysis. Duplicate chemical analyses of samples from a typical 1000 gram batch are shown in Table No. V.

3. Reaction of Ammonium Diuranate, Carbon and Nitrogen

The synthesis of UC by the reaction of ammonium diuranate and carbon has already been discussed. The reactions involved in the preparation of UN by nitriding a mixture of ammonium diuranate and carbon were assumed to be as follows:

$$9(NH_4)_2U_2O_7 \longrightarrow 2N_2 + 14NH_3 + 6U_3O_8 + 15H_2O$$

$$2U_3O_8 + 16C + 3N_2 \longrightarrow 6UN + 16CO$$

A stoichiometric mixture of ammonium diuranate and carbon, based upon the above equations, was heated for 4 hours at 1700°C. in flowing nitrogen and then allowed to cool in nitrogen. X-ray analysis of the product indicated that the major phase was U_2N_3 which, as has been shown, can be converted to UN by vacuum treatment at about 1400°C. However, in addition to the nitride, the product contained considerable carbon,as is seen by the following chemical analysis:

	%
Uranium	89.82
Nitrogen	7.47
Free Carbon	1.01
Combined Carbon	0.29

Because of the excess carbon in the product, it is evident that the reaction did not proceed as outlined in the above equations. The results were much the same as previously obtained when a stoichiometric mixture of U_3O_8 and carbon was nitrided under similar conditions;

in both instances the product contained an excess of carbon (See Table No. III, Experiment 4). As previously mentioned, the explanation is probably that U_3O_8 does not react completely with carbon under the conditions of the experiments but is partially thermally decomposed to UO_2 which then requires less carbon. There are, of course, other complicating factors in the case of the decomposition of ammonium diuranate, as for example, the presence of water vapor and hydrogen. For the above reasons, and because of limited time, it was decided to do no further work on this process.

C. Synthesis of Uranium Silicide (U_3Si_2)

The uranium silicide, U_3Si_2, was chosen for study after considering several factors. The phase diagram for the uranium-silicon system (Figure 7) discloses five compounds with melting points above 1300°C. Of these, U_3Si_2 has the highest uranium density and the second highest melting point (see also Table No. VI).

Two general methods for the preparation of U_3Si_2 were considered: (1) the reaction of elemental uranium and silicon, and (2) the reaction of UO_2 with compounds of silicon or with silicon and carbon. The chief emphasis in the present work has been on the former method.

1. Preparation of U_3Si_2 by Reaction of Uranium and Silicon

The uranium was similar to that used in preparing uranium nitride; it was obtained from National Lead Company in the form of 100 to 250 mesh shot and treated with dilute nitric acid, followed by washing with distilled water and acetone, to remove the oxide film. The silicon, in the form of 325 mesh powder, was purchased from Union Carbide Metals Company and had a purity of 99.7 percent. Stoichiometric amounts of uranium and silicon were prepared for reaction by milling the two powders in a rubber-lined ball mill with stainless steel balls; an inert atmosphere was, of course, maintained in the ball mill.

Initial experiments were made as follows: stoichiometric mixtures of uranium and silicon were placed in crucibles of alumina, siliconized graphite, or boron nitride and heated in an inert atmosphere (argon) to temperatures of the order of 1750°C., held for periods up to 30 minutes, and then allowed to cool slowly to room temperature. In all such experiments the product consisted of a mixture of silicides,

TABLE NO. V

Duplicate Chemical Analyses of Typical 1000 Gram Batch of UN

Component	Sample No. 1 %	Sample No. 2 %
Uranium	94.28	94.27
Nitrogen	(5.05*	5.03*
	(5.5 **	5.6 **
Total Carbon	0.14	0.11
Iron	0.04	0.03
Oxygen	-	0.08***

* Results from Carborundum Laboratory by alkali fusion.
** Results from National Research Corporation by the Kjeldahl method.
*** Determined by the National Research Corporation by vacuum fusion.

TABLE NO. VI

Melting Point and Uranium Density for Various Uranium Compounds

Compound	Melting Point, °C.	Literature Reference	Density g./cc.	Weight Fraction Uranium	U Density g./cc.
USi_3	1510	(2)	8.15	0.739	6.02
USi_2	1700	(2)	8.98	0.809	7.26
U_2Si_3	1610	(2)	9.25	0.851	7.97
USi	1575	(2)	10.40	0.895	9.30
U_3Si_2	1665	(2)	12.20	0.927	11.31
U_3Si	930	(2)	15.58	0.961	14.98
U_2N_3	Decomposes 1450	(3)	11.24	0.919	10.33
UN	2630 ± 50	(4)	14.32	0.944	13.52
UC_2	2400 ± 100	(5)	11.68	0.908	10.60
UC	2400 ± 100	(5)	13.63	0.952	12.97
UO_2	2700 ± 50	(6)	10.96	0.882	9.64
U	1133 ± 2	(7)	19.00	1.000	19.00

the principal constituent frequently being USi_2 (see Experiments 1 and 2, Table No. VII). Since USi_2 tended to crystallize more rapidly than U_3Si_2 from melts at 1750°C., experiments were designed to permit rapid quenching of the melt. This was accomplished in the manner indicated in Figure 8. After a temperature of about 1750°C. had been reached and held for several minutes, the hold rod at the top of the furnace (Figure 8) was lifted upwards, permitting the crucible to spill its contents to the cold end of the furnace tube, thereby quenching the product. Numerous melts made in this way gave consistently a product which x-ray analysis indicated to be principally U_3Si_2 (as an example, see Experiment 3, Table No. VII).

Concurrently with the above work, some synthesis experiments were carried out at lower temperatures. It was observed that the reaction between uranium and silicon went rapidly to essential completion in the range of 1500 to 1550°C. and could be cooled slowly from such temperatures to give U_3Si_2 as the principal product. The experiments were carried out successfully, both in vacuum and in an inert atmosphere (see Experiments 4 and 5, Table No. VII). However, it appears that the latter method may be preferable since U_3Si_2 has shown some tendency to instability in vacuum at temperatures slightly higher than 1550°C. Thus, when U_3Si_2 was heated to 1600°C. in a vacuum there was considerable weight loss and x-ray analysis of the condensed vapors showed the presence of several silicides and free silicon.

The U_3Si_2 made by either quenching from 1700-1750°C. or slow cooling from 1500-1550°C. normally had weak x-ray patterns for UO_2 and silicon. It was found that the synthesis of U_3Si_2 in larger batches reduced the oxygen content of the product to a comparatively low level (compare Experiments 4 and 5, Table No. VII).

To investigate the cause of apparent free silicon in the product, syntheses were made using silicon in deficient, excess, and stoichiometric amounts. X-ray reports indicated free silicon in all cases. However, metallographic examination of the products showed single phase material when stoichiometric quantities had been used. The inconsistency was resolved by recalculation of the x-ray diffraction pattern for U_3Si_2, showing that some lines in the patterns are common to both Si and U_3Si_2.

A variety of crucible materials were examined for use in the synthesis of U_3Si_2. These included alumina, aluminum nitride, graphite, siliconized graphite, boron nitride, beryllia, magnesia,

TABLE NO. VII

Summary of Some Typical Experiments on the Synthesis of U_3Si_2 from U + Si

Experiment No.	Amount of Product, g.	Max. Temp. °C.	Time at Max. Temp. min.	Crucible Material	Furnace Type	Atmosphere	X-Ray Analysis		Remarks
1	50	1750	30	Al_2O_3	Induction	Argon	Major Mod. Weak	USi_2 U_3Si U_3O_8 and Si	Cooled slowly
2	50	1750	5	BN	Induction	Argon	Mod. Mod. Faint	USi_2 U_3Si_2 UO_2 and Si	Cooled slowly
3	50	1800	5	BN	Induction	Argon	Major Weak	U_3Si_2 UO_2 and Si	Quenched from 1800°C.
4	50	1550	0	MgO	Muffle	Argon	Major Weak Faint	U_3Si_2 Si UO_2	Cooled slowly
5	500	1550	0	MgO	Induction	Vacuum	Major Weak	U_3Si_2 Si	Cooled slowly. *Oxygen 0.07%
6	50	1200		MgO	Induction	Vacuum	Mod. Weak to Mod. Indication of	U_3Si_2 USi_2 and UO_2 U_3Si	Cooled slowly. Starting materials UH_3 + Si

* Determined by vacuum fusion.
Note: The presence of free silicon in the above products is questionable. See paragraph 4, page 17.

thoria, and tantalum. The most satisfactory materials from the standpoints of non-wetting and freedom from attack by the uranium-silicon compositions were beryllia, thoria, and magnesia. Because of its ready availability, magnesia was chosen as the standard crucible material. The mix reacted markedly with tantalum crucibles.

Most of the U_3Si_2 made for fabrication and physical property tests, to be described later, was synthesized by the non-quenching method: the mixture of the elements was heated in vacuum or inert atmosphere to 1500-1550°C. and allowed to cool to room temperature by simply shutting off the power from the furnace. A typical analysis of one to three pound batches made by this method in the vacuum furnace was as follows:

	%
Uranium	92.32
Silicon	6.96
Carbon	0.14
Oxygen	0.07
Nitrogen	0.03
Iron	0.29

If the vacuum furnace is used for the synthesis of U_3Si_2 it is necessary to control the temperature carefully because of the instability of the compound in vacuum at temperatures slightly higher than 1550°C.

The possibility of preparing U_3Si_2 at temperatures appreciably lower than 1500-1550°C. has also been considered. A few experiments in the vacuum furnace at 1200°C. indicated that the reaction of silicon powder and 100-250 mesh uranium did not go to completion, at least in a short hold time. When the 100-250 mesh uranium was first hydrided to produce a finer powder, single phase U_3Si_2 was still not obtained. In these experiments, it was observed that when compacts of uranium and silicon are carefully heated, an exothermic reaction takes place at about 875°C.

2. Preparation of U_3Si_2 by Reaction of Uranium Dioxide, Silicon Carbide and Carbon

Exploratory experiments were first made to determine if USi_2 could be prepared from silicon carbide according to the equation

$$2SiC + UO_2 \longrightarrow USi_2 + 2CO$$

Minus 25 micron powders were mixed, pressed into pellets and heated in a ceramic tube furnace in an argon atmosphere. X-ray analysis of the product showed a strong pattern for USi_2 after 15 hours at 1500°C., or after one hour at 1700°C.

One experiment was designed to produce U_3Si_2 according to the reaction

$$3UO_2 + 2SiC + 4C \longrightarrow U_3Si_2 + 6CO$$

In this case the pressed pellet was heated for one-half hour at 1700°C. X-ray examination indicated the product to be USi_2, UO_2 and SiC. Because of time limitations and because initial experiments were not especially encouraging, no further work was done on this method.

III. FABRICATION EXPERIMENTS

In the present study, fabrication experiments were limited to powder metallurgy techniques. Cold pressing and sintering were emphasized, although preliminary results obtained by reaction hot-pressing of UC and U_3Si_2 were encouraging.

A. Fabrication of Uranium Monocarbide

1. Cold Pressing and Sintering

The UC used in the fabrication studies was prepared by reacting stoichiometric amounts of UO_2 and C, as described in Part II of this report. The reaction product, in the form of clinker, was crushed to minus 80 mesh in an inert atmosphere and then reduced to fine particle size by dry milling in an inert atmosphere in a rubber-lined ball mill with stainless steel balls. Numerous batches of powder were produced; most of these were milled to an average particle size of less than 2 microns. The analysis of various batches of UC powder fell within the following limits:

	%
Uranium	94.50 - 95.40
Carbon	4.65 - 4.90
Oxygen	0.05 - 0.35
Nitrogen	trace - 0.10
Iron	trace - 0.10

Several variables in fabrication were studied; as a result, the following procedure was developed for producing high density specimens:

Uranium monocarbide, having an average particle size of less than 2 microns, was cold pressed at about 20,000 pounds per square inch using 0.5 percent Carbowax (based on the weight of UC) dissolved in trichlorethylene as the temporary binder. The trichlorethylene was vaporized from the specimens at room temperature in an inert atmosphere. The specimens were then placed in tantalum-lined graphite crucibles and the Carbowax removed by heating at the rate of 50°C. per hour to 600°C. and then at 200°C. per hour to 1400°C. After cooling, the crucibles were placed in an induction heated vacuum furnace, the temperature raised to 1850°C. in about one hour and held at the maximum temperature for one hour. The resulting specimens had densities ranging from 92 to 96 percent of theoretical, there being some variations in density from batch to batch as well as some variation within the same batch.

Of the factors which affect the sinterability of UC, particle size appears to be quite important. The highest densities were obtained by sintering powders having an average particle size of less than two microns. It was necessary to ball mill minus 80 mesh UC for at least 24 hours to obtain high density specimens. Longer ball milling times, however, did not necessarily improve sintered density. These points are illustrated in Tables No. VIII and IX.

One-half percent Carbowax 6000 was found to be a satisfactory binder. Results obtained with three different amounts of Carbowax are compared in Table No. X.

In a study of cold forming pressures, no improvement in sintered density was obtained by using pressures in excess of 20,000 to 30,000 pounds per square inch. Some increase in unfired bulk density, however, was found at higher pressures (see Table No. XI). It should be emphasized that these data may not be typical of coarse powders, or powders prepared by other procedures.

The effect of time and temperature of sintering on the density of UC pellets is seen in Table No. XII. From these data it appears that a temperature of 1850°C. held for one hour produces the best results; higher temperatures or longer times give a product containing more UC_2 contamination with no improvement in density.

TABLE NO. VIII

Effect of Particle Size on Density of Sintered UC

Particle Size	Density in g./cc. on Sintering at 1850°C.	1950°C.	2050°C.
-80 Mesh	-	10.30	9.93
2 Microns	-	10.65	10.60
0.5 Microns	12.50	-	-

TABLE NO. IX

Effect of Milling Time on Density of Sintered UC

Milling Time, hr.	24	48	72
Unfired Bulk Density, g/cc	8.75	8.70	8.80
Sintered Bulk Density, g/cc	12.83	12.67	12.69

TABLE NO. X

Effect of Amount of Binder on Density of UC

Carbowax, %	0.25	0.50	0.75
Unfired Bulk Density, g/cc	8.59	8.75	8.44
Sintered Bulk Density, g/cc	12.40	12.83	12.53

TABLE NO. XI

Effect of Cold Forming Pressure on Density of UC

UC Batch No.	Forming Pressure psi.	Unfired Density g./cc.	Sintered Density g./cc.
1	15,000	8.76	11.21
	20,000	8.87	10.95
	30,000	9.02	11.29
	40,000	9.02	11.11
2	28,000	8.93	12.30
	56,000	9.37	12.30
	84,000	9.50	12.30

TABLE NO. XII

Effect of Time and Temperature of Sintering on Density of UC Pellets

Temperature °C.	Sintering Time, hr.	Density, g./cc.	X-Ray Analysis
1750	1	11.85	Major UC, very faint UO_2
1850	1	12.49	Major UC, very faint UO_2 and UC_2
1850	3	12.22	Major UC, weak to moderate UC_2
2100	1/2	12.42	Major UC, weak to moderate UC_2

In these experiments, the Carbowax binder was removed by careful heating in a ceramic tube muffle furnace rather than in the induction vacuum furnace where the final sintering was done. This was because the rate of heating in the induction furnace could not be controlled accurately enough to prevent rupturing the specimens by too rapid removal of the binder.

In the early experiments, the specimens were contained in graphite crucibles during sintering. However, some tendency to UC_2 formation was noted, especially on the surface of the pieces. For this reason tantalum-lined graphite crucibles were adopted as containers in the latter stages of this investigation, and were effective in preventing UC_2 formation.

In the present work, UC specimens have been fabricated in the following shapes and sizes: cylinders, 0.2 inches by 0.2 inches, 0.5 inches by 0.5 inches, and 1 inch by 1 inch; also, bars 1/4 inch by 1/2 inch by 3 inches.

Metallographic examination of sintered UC specimens frequently showed indications of uranium metal at the grain boundaries, and trace amounts of UC_2 and a third phase believed to be UO_2. Photomicrographs of representative polished sections are seen in Figures 9 and 10.

2. Reaction Hot Pressing

This method consists of reacting stoichiometric amounts of fine uranium and carbon powders while applying pressure. It had previously been explored by Dubuisson et al.[8] who used uranium powder prepared by the calcium reduction of UO_2. The source of uranium, in the present investigation, was 100-250 mesh shot obtained from National Lead Company. In several experiments the uranium shot was used as received, but in two hot pressings the shot was first hydrided to produce a finer powder. In all experiments, the carbon was minus 2 micron powder having an ash content of about 0.05 percent.

The usual fabrication procedure was as follows: The mixture of powders was ball-milled for 24 hours in a rubber-lined mill with stainless steel balls and then pressed in graphite dies at 1,500 psi. at maximum temperatures of 1000 to 1400°C. A schematic drawing of the hot pressing equipment is shown in Figure 11.

Erratic results were obtained in the experiments when the 100-250 mesh uranium was used as received, probably because of non-uniformity of the uranium-carbon mixtures. In one such experiment, the heating cycle was one hour at 800°C., raised to 1400°C. in two hours and maintained there for two hours. The pellet that was obtained had a density of 13.3 grams per cubic centimeter. X-ray and chemical analyses were as follows:

X-Ray Analysis	Chemical Analysis, %	
Major UC	Uranium	95.26
Very faint indications of UO_2	Total Carbon	4.46
	Uncombined Carbon	0.13
	Iron	0.04
	Nitrogen	0.10

Metallographic examination of a polished section of the pellet showed considerable uranium metal which was not distributed uniformly.

Two hot pressings were carried out using fine uranium metal powder produced by hydriding the metal shot. In these experiments the metal powder and carbon were mixed in a Spex mixer by rapid vibratory motion. In the first hot pressing the temperature was held at 800°C. for one hour, then raised to 1200°C. and held for one hour. The resulting pellet had a density of 13.05 grams per cubic centimeter; metallographic examination revealed uranium metal located in pools which were more numerous towards the outside of the pellet. The second hot pressing was carried out by holding at 800°C. for one hour, followed by pressing at 1000°C. for 4-1/2 hours. The resulting pellet had a density of 13.19 grams per cubic centimeter; metallographic examination revealed less free uranium metal and a smaller grain size than in the previous pellet. A photograph of a polished section of this pellet is shown as Figure 12.

B. Fabrication of Uranium Nitride by Cold Pressing and Sintering

The UN used in these experiments was made by nitriding uranium as described in Part II of this report. The powder was pyrophoric and great care was required in handling it to avoid oxidation.

The optimum procedure developed for the fabrication of UN by cold pressing and sintering was essentially the same as that for the fabrication of UC previously described. The powder was reduced to minus 2 micron particles by ball milling for at least 24 hours in a rubber-lined mill with stainless steel balls. The milled powder was then cold pressed at 12,000 pounds per square inch, using 0.5 percent Carbowax 6000 as the temporary binder. The Carbowax was removed by carefully heating in flowing argon as described under the fabrication of UC. The final sintering was done by heating in the vacuum furnace for one hour at 1850°C. As with UC, the most satisfactory container material for use in sintering UN was tantalum-lined graphite crucibles.

The density of pieces fabricated by the above procedure ranged from about 12.0 to 13.6 grams per cubic centimeter, or about 84 to 95 percent of theoretical based upon 14.31 grams per cubic centimeter for pure UN. Density varied from batch to batch of UN powder used for fabrication, and although x-ray examination indicated single phase UN for the various batches of powder, chemical analysis showed a deficiency of nitrogen in the most sinterable powders. Furthermore, metallographic examination indicated the presence of metal in the highest density specimen (Figure 13), and unquestioned single phase UN only in specimens having a maximum density of about 12.0 grams per cubic centimeter (Figure 14). Specimens of intermediate density appeared to have a second phase which could not be identified. This possible second phase was somewhat darker than UN, under reflected light, and tended to etch more readily with acids (Figure 15). Variation of density of sintered UN with nitrogen content is seen in Table No. XIII.

Uranium mononitride was also sintered successfully in an alumina tube muffle furnace (Figure 2) in flowing argon or helium. However, it was more difficult to prevent oxidation in this case, and the required temperature of 1850°C. was difficult to maintain because of the refractory limitations of the alumina muffle.

In addition to composition, the effect of the following variables on sintered density were studied: particle size of the powder, cold forming pressure, and sintering temperature.

TABLE NO. XIII

Variation of Density of Sintered UN with Nitrogen Content

Experiment No.	Nitrogen Content %	Density g/cc.	Metallographic Examination
1	4.6	13.2	UN + possible 2nd phase
2	4.7	13.6	UN + U
3	4.8	12.8	UN + possible 2nd phase
4	5.1	12.9	UN + possible 2nd phase
5	5.6	12.0	Single phase UN

As previously stated, the best procedure developed for producing UN from uranium was: (1) hydride 100-250 mesh uranium shot; (2) decompose the resulting hydride and nitride the product at about 800°C.; and (3) reduce the higher nitrides to UN by vacuum treatment at 1400°C. This procedure resulted in UN powder having an average particle size of 6 to 8 microns. The average density obtained on sintering such material was about 10 grams per cubic centimeter; however, when the powder was first reduced to an average particle size of about 1.5 microns by milling, the density obtained on sintering under the same conditions was 12.6 grams per cubic centimeter. These experiments are summarized in Table No. XIV.

The pressure chosen for cold forming was 12,000 pounds per square inch. This choice was based upon experiments which showed that pressures higher than about 10,000 pounds per square inch did not result in higher density when using milled minus 2 micron UN. In fact higher pressures sometimes resulted in pieces with lamination cracks which were evident only after sintering. The effect of cold forming pressure on the density of sintered UN is seen in Table No. XV.

No improvement in the density of fabricated UN was achieved by sintering at temperatures higher than 1850°C. Thus, when single phase UN, having essentially theoretical composition, was vacuum sintered for one hour at 1850°C., 1950°C., or 2100°C., the resulting densities were respectively as follows: 12.0 grams per cubic centimeter, 11.3 grams per cubic centimeter, and 12.1 grams per cubic centimeter. Metallographic examination of the sintered pellets indicated that the composition was still single phase UN in each case after sintering.

C. Fabrication of Uranium Silicide (U_3Si_2)

1. Cold Pressing and Sintering

The procedure used in cold pressing U_3Si_2 was, in general, similar to that already described for UC and UN. The product from the reaction of U and Si (see Part II of this report) was crushed and milled to an average particle size of less than 2 microns. This required milling for at least 48 hours in a rubber-lined mill with stainless steel balls. Forming pressures of from 5,000 to 20,000 pounds per square inch were tried, using Carbowax 6000 as the temporary binder; however, it was found that a pressure

TABLE NO. XIV

Effect of Milling Time and Particle Size on the Density of Sintered UN

Experiment No.	Milling Time, hr.	Average Particle Size, micron	Density	
			g/cc.	% of Theoretical
1	0	6-8	10.0	70
2	56	-	12.7	89
3	72	1-2	12.6	88

TABLE NO. XV

Effect of Cold Forming Pressure on the Density of Sintered UN

Experiment No.	Cold Forming Pressure, psi.	Density Before Sintering		Density After Sintering	
		g/cc.	% Theoretical	g/cc.	% Theoretical
1	10,000	-	-	13.0	90.9
2	12,000	8.9	62	12.7	98.9
3	15,000	-	-	13.1	91.6
4	16,000	9.3	65	12.7	88.9
5	26,000	-	-	12.9	90.3

of 6,000 pounds per square inch was adequate to give maximum sintered density. High forming pressures (15,000-20,000 pounds per square inch) frequently caused lamination cracks in the sintered pellets.

Both removal of the binder and sintering were done in a ceramic tube muffle furnace (Figure 2) in flowing argon. The preferred heating schedule was as follows: temperature raised at the rate of 50°C. per hour to 600°C., then 200°C. per hour to 1400°C. and held for one hour. Of several container materials tried, tantalum-lined graphite crucibles were found to be the most suitable, especially from the standpoint of protecting the silicide from oxidation during sintering.

The fabrication procedure outlined above resulted in sintered U_3Si_2 specimens having a density of 11.8 to 12.0 grams per cubic centimeter, or about 96.8 to 98.4 percent of theoretical. A polished section of typical high density specimen of U_3Si_2 is seen in Figure 16.

2. Reaction Hot Pressing

Preliminary experiments were carried out on the simultaneous synthesis and fabrication of U_3Si_2 by reaction hot pressing. Two powder mixtures of reactants were used: (1) 100 to 250 mesh uranium shot and minus 325 mesh silicon, and (2) 100 to 250 mesh uranium shot and minus 200 mesh uranium trisilicide (USi_3). The experiments were made at temperatures ranging from 925 to 1500°C. using die materials of graphite, aluminum nitride or boron nitride. The hot pressing equipment was similar to that used for reaction hot pressing of UC (Figure 11).

These experiments are summarized in Table No. XVI. The results indicate that it is possible to form U_3Si_2 at temperatures as low as 925°C.; that graphite is not a satisfactory die material except possibly at low temperatures (925°C.) where long hold periods are necessary; and that the method has considerable promise if a satisfactory die material is used. Some possible good die materials may be aluminum nitride, magnesia, and beryllia.

TABLE NO. XVI

Synthesis and Fabrication of U_3Si_2 by Reaction Hot Pressing

Experiment No.	Reactants	Temperature °C.	Time at Max. Temp., min.	Pressure, psi.	Die Material	X-Ray Analysis	Density, g/cc.
1	3U + 2Si	925	5	1500	Graphite	Major USi Mod. U_3Si_2 Weak UO_2 & Si	11.4
2	3U + 2Si	925	60	1000	Graphite	Major U_3Si_2 Weak Si	11.1
3	3U + 2Si	925	30	1000	Aluminum Nitride	Major U_3Si_2 Weak to Mod. Si	10.5
4	7U + 2USi_3	1150	5	1500	Graphite	Major U_3Si_2 Mod. Si Weak UO_2 & UC	11.0
5	3U + 2Si	1300	3	1500	Graphite	Mod. U_3Si_2 & SiC Weak UO_2 & Si Faint USi_3	-
6	3U + 2Si	1500	5	1000	Boron Nitride	Major U_3Si_2 Weak to Mod. Si	11.2
7	U_3Si_2*	1450	30	1000	Graphite	Major USi_2 Weak to Mod. U_3Si_2 and UO_2 Indication of USi_3	10.0

* X-ray analysis: Major U_3Si_2; Indications of UO_2 and Si

IV. PHYSICAL PROPERTIES OF URANIUM MONOCARBIDE, URANIUM MONONITRIDE AND URANIUM SILICIDE (U_3Si_2)

A. Summary of Properties

The following properties were studied: thermal expansion, thermal conductivity, modulus of rupture, Young's modulus, shear modulus, electrical resistivity, resistance to thermal cycling, and stability in water. The results are briefly summarized in Table No. XVII and are described in more detail in the sections which follow.

B. Thermal Expansion

Thermal expansion was determined by a dilatometer method in an argon atmosphere. The apparatus is illustrated in Figure 17. The test specimen, a bar 3 inches by 1/2-inch by 1/4-inch, rests on the closed end of an impermeable silicon carbide tube. A high density silicon carbide rod transmits the sample expansion to an Ames micrometer dial located on a water-cooled flange. The dilatometer assembly is closed off with a bell jar resting on the water-cooled flange. After evacuating the apparatus, a flowing argon atmosphere is established to protect the sample from oxidation.

Expansion measurements were made on two specimens each of UC, UN and U_3Si_2. The specimens differ somewhat in density as indicated below:

Material	Density, g/cc. Sample 1	Sample 2
UC	12.68	11.30
UN	11.35	12.00
U_3Si_2	11.12	11.45

Two series of measurements were made on each of the No. 1 samples and one on the No. 2 samples, except in the case of UN where only one series of measurements was made on each sample. There was no significant difference in the results obtained with the No. 1 and No. 2 specimens, as is indicated by Figure 18. Table No. XVIII shows the average coefficient of thermal expansion of the three materials at various temperature intervals.

TABLE NO. XVII

Summary of Physical Properties of UC, UN, and U_3Si_2

Property		UC	UN	U_3Si_2
Average density of specimens tested, % theoretical		90	81	92
Average thermal expansion from 25 to 1200°C., cm/cm/°C.		11.43×10^{-6}	9.70×10^{-6}	14.99×10^{-6}
Thermal conductivity at 800°C., cal/cm^2/cm/sec/°C.		0.07	0.13	0.06
Electrical resistivity at room temperature, ohm-cm		5.01×10^{-5}	2.08×10^{-4}	1.50×10^{-4}
Young's modulus at room temperature, psi.		25.0×10^{6}	21.6×10^{6}	11.3×10^{5}
Shear modulus at room temperature, psi		9.7×10^{6}	8.7×10^{6}	4.8×10^{6}
Poisson's ratio at room temperature		0.29	0.24	0.17
Modulus of Rupture at (psi)	25°C.	23,000	10,500	12,500
	600°C.	-	-	11,300
	800°C.	17,600	11,200	Deforms
	1000°C.	10,000	-	-
	1200°C.	Deforms	19,300	-
	1400°C.	-	13,700	-
	1600°C.	-	Deforms	-
Stability in water at	100°C.	Disintegrates	Only slight reaction	Only slight reaction
	200°C.	-	Disintegrates	Only slight reaction

TABLE NO. XVIII

Thermal Expansion of UC, UN and U_3Si_2

Temperature Interval, °C.	Average Coefficient of Thermal Expansion, cm/cm/°C.		
	UC	UN	U_3Si_2
25 - 200	9.47	8.55	13.54
25 - 400	10.30	8.71	14.03
25 - 600	10.68	8.90	14.32
25 - 800	11.01	9.10	14.57
25 - 1000	11.23	9.30	14.85
25 - 1200	11.43	9.70	14.99

C. Thermal Conductivity

The thermal conductivity data reported in this section were obtained on a single specimen each of UC, UN and U_3Si_2. These values will be checked by additional experiments and reported at a later date; therefore, the present data are to be considered as preliminary only.

Thermal conductivity was measured by a comparative method using equipment similar to that designed by Francl and Kingery[9] of the Massachusetts Institute of Technology (see Figure 19). The standard for comparison was nickel, obtained from the International Nickel Company. The two standards and the test specimen were right cylinders, one inch in diameter by one inch high, machined to dimensional tolerances of plus or minus 0.001 inch.

Thermal gradient was determined by a pair of thermocouples in each standard and test specimen. The thermocouples in each cylinder were 0.75 inches apart and positioned at the center of the diameter of the cylinder by inserting them in holes about 0.035 inches in diameter. The ceramic tube surrounding the sample-standard assembly was heated to approximately the same temperature as the assembly to minimize lateral heat flow; this was accomplished by five independently-controlled platinum heaters. The equipment was enclosed in a bell jar and thermal conductivity measurements made in a vacuum.

Preliminary values for the thermal conductivity of UC, UN and U_3Si_2 are reported in Figures 20, 21 and 22, respectively. Densities of the test specimens, in terms of percent of theoretical, were as follows: UC, 88.3; UN, 81.0; and U_3Si_2, 92.2. Values were also calculated for 100 percent dense specimens by the formula[10]

$$K_S = \frac{K_m}{(1-P_v)}$$

where K_S is the thermal conductivity at zero porosity; K_m, measured thermal conductivity, and P_v, volume pore fraction. All values reported are based upon a comparison with the thermal conductivity data for nickel as determined by Francl and Kingery[10] and shown in Figure 20.

D. Modulus of Rupture

Modulus of rupture determinations were carried out at room temperature using a Universal testing machine with a loading rate of 0.05 inches per minute. Determinations at higher temperatures were made using the apparatus illustrated in Figures 23 and 24. The sample holder, Figure 23, consists of two pieces of graphite which fit together along eight bearing surfaces to insure correct alignment. The test specimen is supported by two graphite pins in the lower piece; pressure is applied by two graphite pins in the upper piece, thus subjecting the sample to four-point loading.

The test specimens for both room temperature and high temperature determinations were bars 3 inches by 1/2-inch by 1/4-inch. The span was 2-1/2 inches.

The graphite assembly containing the test bar was placed in an inductively-heated furnace as shown in Figure 24. Temperature was determined by sighting on the edge of the sample holder with an optical pyrometer. An argon atmosphere was maintained in the furnace during the determination and cooling periods. While this did not protect the samples completely from oxidation, only thin oxide films were found on the samples after cooling.

In the tests at elevated temperatures it was found that specimens of UC, UN and U_3Si_2 deformed under load when certain temperatures had been reached. These temperatures were as follows: UC, 1200°C.; UN, 1600°C.; and U_3Si_2, 800°C. Examples of deformed

UC and UN bars are seen in Figure 25. Metallographic examination of polished sections of such bars indicated essentially single phase composition (Figures 9a,14 and 16); therefore, it appears that deformation is not caused by the presence of a metal matrix in these pieces but is a fundamental property of the compounds.

The behavior of U_3Si_2 in the high temperature modulus of rupture tests was unique, although its behavior at room temperature was quite normal. At 800°C. the bars deformed gradually and showed no evidence of breaking during the application of pressure. However, after the furnace had cooled, it was found that the bar had broken into many pieces (see Figure 26). At 600°C., a normal sharp break was obtained, but again after cooling, the bar was found to have broken into many pieces. Thermal expansion studies of U_3Si_2 showed no sudden volume changes on heating gradually to 1200°C., as might have been expected had a phase change taken place. Also, when a test bar of U_3Si_2 was heated and cooled in a graphite crucible in a ceramic tube furnace in an inert atmosphere, no cracking occurred; but when the same cycle of heating and cooling was carried out in the modulus of rupture equipment, even without application of pressure, the characteristic cracking of the bar shown in Figure 26 was observed. It is believed that this disintegration of the U_3Si_2 bars in the modulus of rupture equipment was the result of partial oxidation during slow cooling of the furnace. N. R. Koenig[11] has noted catastrophic cracking of U_3Si_2 specimens as the result of oxidation.

Results of modulus of rupture determinations are shown in Table No. XIX.

E. Young's Modulus, Shear Modulus and Poisson's Ratio

Young's modulus and shear modulus were determined by a sonic method on sintered bars of UC, UN and U_3Si_2 having nominal dimensions of 3 inches by 1/2-inch by 1/4-inch. Determinations were made at room temperature only.

TABLE NO. XIX

Modulus of Rupture of UC, UN and U_3Si_2

Material	Temperature, °C.	No. of Bars Tested	Density, % Theoretical	Average Modulus of Rupture psi.	Range, psi.
UC	25	5	90-94	23,000	15,400-33,500
	800	3	84-87	17,600	15,000-20,000
	1000	1	83	10,000	-
	1200	2	83-91	Bars deformed under load	
UN	25	3	81-83	10,500	10,200-10,900
	800	4	79-84	11,200	8,000-14,500
	1200	1	81	19,300	-
	1400	1	78	13,700	-
	1600	2	82-84	Bars deformed under load	
U_3Si_2	25	5	92-98	12,500	10,300-17,600
	600	4	90-94	11,300	8,700-17,700
	800	4	93-98	Bars deformed under load	

Frequency measurements were made on bars which were suspended between elastic bands located at the nodes, so as to not dampen the vibrations. The bars were driven with a cutting head driver of type A41-8, manufactured by the Astatic Corporation. The vibrations were detected by means of a microphone held directly above the specimen. Young's modulus was calculated from the frequency of the first mode of flexural vibration; shear modulus, from the frequency of vibration in the torsional mode. Methods of calculation were based on equations developed by Pickett[12]. Poisson's ratio was calculated from Young's modulus and shear modulus by the equation

$$\text{Poisson's ratio} = \frac{E}{2G} - 1$$

where E is Young's modulus and G is shear modulus.

In the case of each compound, data were obtained on bars representing a range in density. In general, there appeared to be a linear relationship between Young's modulus and porosity and also between shear modulus and porosity, at least in the density ranges involved in the present investigation. This can be seen by inspection of Figures 27 through 32.

It will be noted that there is considerable dispersion in the points on the above graphs, especially in the case of U_3Si_2. It is believed that this is mainly due to variations in the cross-section dimensions along the length of a specific bar. The bars were not machined, but used as sintered.

Poisson's ratio for UC and UN was calculated from the data in Figures 27 through 30. In these calculations, values for Young's modulus and shear modulus were taken from the straight line graphs at specific densities. Since the dispersion of points was considerably greater in the case of U_3Si_2, calculations of Poisson's ratio for different densities of U_3Si_2 were made from values of Young's modulus and shear modulus obtained on each bar. (Points having corresponding numbers in Figures 31 and 32 represent data on the same bar). The results for UC, UN and U_3Si_2, shown in Table No. XX, indicate that Poisson's ratio is higher at higher densities.

TABLE NO. XX

Variation of Poisson's Ratio for UC, UN and U_3Si_2 With Density

Density, % of Theoretical	Poisson's Ratio*	
	UC	UN
75	-	0.215
80	0.182	0.240
85	0.241	0.250
90	0.286	0.260
95	0.304	-

*Calculated from graphs of Figures 27 through 30.

Bar No.	Density, % of Theoretical	Poisson's Ratio**
		U_3Si_2
1	90.2	0.161
2	93.4	0.181
3	97.1	0.179
4	97.1	0.185
5	97.7	0.185

**Calculated from data on individual bars. (See numbered points of Figures 31 and 32).

F. Electrical Resistivity

Electrical resistivity measurements were made on UC, UN and U_3Si_2 at room temperature, using sintered bars, 3 inches by 1/2-inch by 1/4-inch. The samples were prepared for measurements by abrading the surfaces of the bars under kerosene to remove any interfering oxide film. Resistance measurements were made on a Kelvin Bridge Ohmmeter (Leeds and Northrup Model 4285). Results are shown in Table No. XXI.

TABLE NO. XXI

Electrical Resistivity of UC, UN and U_3Si_2 at Room Temperature

Material	Density g/cc.	Density % Theoretical	Electrical Resistivity ohm-cm
UC	12.28	90.10	5.00×10^{-5}
UC	12.05	88.41	5.02×10^{-5}
UN	11.83	82.63	2.08×10^{-4}
UN	11.80	82.42	2.06×10^{-4}
UN	11.58	80.90	2.10×10^{-4}
U_3Si_2	11.45	93.85	1.49×10^{-4}
U_3Si_2	11.20	91.80	1.50×10^{-4}

G. Resistance to Thermal Cycling

The resistance of UC, UN, U_3Si_2 and UO_2 to mild thermal cycling was studied. The specimens were pellets, 1/2-inch diameter by 1/2-inch long, having the following densities:

Material	Density g/cc	Density % Theoretical
UC	12.7	93.2
UN	11.3	78.8
U_3Si_2	11.6	95.2
UO_2	10.4	94.8

The heating was done in a tube furnace attached to a glove box (Figure 33), making possible heating and cooling in an inert atmosphere.

The pellets were placed in a stainless steel boat at room temperature and plunged into the hot zone of the furnace at 1200°C. The temperature of the pellets rose to 1100°C. in about 2-1/2 minutes. The pellets were kept in the furnace for 10 minutes and then quickly withdrawn and cooled with a stream of argon at room temperature. The pellets cooled to below red heat in about one minute and to room temperature in about ten minutes. The above procedure was repeated for 18 cycles after which the pellets were examined. There was no evidence of cracking or spalling of any pellets, although the surfaces had become slightly darkened, probably as the result of superficial oxidation. The pellets were sectioned and examined metallographically but no significant change in microstructure was detected.

H. Stability in Water

The specimens tested were bars, 1/4-inch by 1/2-inch by 3/4-inch.

UC reacted slowly with water at room temperature, as evidenced by rate of formation of bubbles; at 40°C. the rate was vigorous and the bars disintegrated in a few minutes.

UN and U_3Si_2 did not show visible evidence of reaction with water at room temperature and reacted only slightly with water at 100°C. after 16 days' exposure. However, samples of UN immersed in distilled water at 200°C. for 14 days completely disintegrated. In contrast, U_3Si_2 showed only slight evidence of reaction with water at 200°C. The test at 200°C. was conducted as follows: The specimens were placed in pyrex glass tubes which were about one-third full of distilled water. The tubes were sealed, placed in steel cylinders and the cylinders heated to 200°C. in an oven for the specified period, removed from the oven, cooled and the specimens inspected.

The results of stability tests of UC, UN and U_3Si_2 in water are summarized in Table No. XXII.

TABLE NO. XXII

Stability of UC, UN and U_3Si_2 in Water

Test No.	Material	Density g/cc.	Temperature, °C.	Exposure Time, days	Weight Change, %
1	UC	12.3	25	0	Slow bubble formation
2	UC	12.3	40	0	Reacts vigorously
3	UN	11.7	100	14	0.034 gain
4	UN	11.8	100	14	0.044 gain
5	UN	11.7	200	14	Complete disintegration
6	UN	11.8	200	14	Complete disintegration
7	U_3Si_2	11.8	100	16	0.029 loss
8	U_3Si_2	11.8	100	16	0.042 loss
9	U_3Si_2	11.3	100	5	0.001 loss
10	U_3Si_2	11.3	200	4	0.020 loss

V. SUMMARY

Uranium monocarbide of 97 to 99 percent purity was prepared by carbon reduction of UO_2, and fabricated by cold pressing and sintering into fuel pellets with densities ranging from 92 to 96 percent of theoretical. Reaction hot pressing was also used to produce pellets of about 95 percent theoretical density.

Uranium nitride was synthesized by (1) nitriding stoichiometric mixtures of UO_2 and carbon and (2) by nitriding uranium metal. Fabrication was by cold pressing and sintering. High density pellets (about 95 percent of theoretical) were obtained only with nitrogen deficient powder; with powder of stoichiometric composition, the maximum density obtained was about 85 percent of theoretical.

Uranium silicide, U_3Si_2, was prepared (1) by quenching melts of uranium and silicon from about 1750°C., or (2) by reacting a mixture of uranium and silicon powders at 1450-1500°C., followed by normal cooling. Pellets of 96 to 98 percent theoretical density were fabricated by cold pressing and sintering. Reaction hot pressing also appeared to be a promising method of forming U_3Si_2 pellets.

Several properties of UC, UN and U_3Si_2 were studied. Of the three compounds, UN has the lowest thermal expansion, the highest strength at temperatures above 1000°C., and the highest thermal conductivity. U_3Si_2 is the most stable in water, and UC, the least. None of these materials, considered as ceramics, appear to be abnormally sensitive to thermal shock.

VI. REFERENCES

1. Joseph J. Katz and Eugene Rabinowitch, "The Chemistry of Uranium," Part I, p. 319, McGraw-Hill Company, Inc. (1951).

2. A. Kaufmann, B. Cullity and G. Britsianes, Uranium-Silicon Alloys, Journal of Metals, 9, Section 2, 23-27 (1952).

3. K. M. Taylor et al., Synthesis and Fabrication of Refractory Uranium Compounds, Second Quarterly Report, U.S. AEC Contract No. AT-(40-1)-2558, p. 4, Sept. 1 to Nov. 30, 1959.

4. Joseph J. Katz and Eugene Rabinowitch, Chemistry of Uranium, Collected Papers, p. 53-66, U.S. AEC, TID-5290 (1958).

5. F. W. Rough and W. Chubb, An Evaluation of Data On Nuclear Carbides, Battelle Memorial Institute Report No. BMI-1441, Contract No. W-7405-eng-92, May 31, 1960.

6. H. W. Newkirk and J. L. Bates, The Melting Points of Uranium Dioxide, Uranium Monocarbide and Uranium Mononitride, HW-59468, General Electric Company, Hanford Atomic Products Operation, Richland, Washington, March 4, 1959.

7. Joseph J. Katz and Eugene Rabinowitch, "The Chemistry of Uranium," Part I, p. 150-152, McGraw-Hill Company, Inc. (1951).

8. J. Dubuisson et al., The Preparation of Uranium-Uranium Carbide Cermets and Stoichiometric Monocarbide by Sintering Under Stress, United Nations Peaceful Uses of Atomic Energy, Proceedings of the Second International Conference, Geneva, 1958, Vol. 6, p. 551; United Nations Publication, Sales No.: 58, IX, 2, Vol. 6.

9. J. Francl and W. D. Kingery, Apparatus for Determining Thermal Conductivity by a Comparative Method, J. Am. Ceram. Soc., 37, No. 2, Part II, 80 (1954).

10. J. Francl and W. D. Kingery, Experimental Investigation of Effect of Porosity on Thermal Conductivity, J. Am. Ceram. Soc., 37, No. 2, 99 (1954).

11. N. R. Koenig, Ceramic and Cermet Fuel Evaluation, Atomics International NAA-SR-Memo-5199, April 20, 1960.

12. G. Pickett, Equations for Computing Elastic Constants from Flexural and Torsional Resonant Frequencies of Vibration of Prisms and Cylinders, ASTM Proc. 45, 846 (1945).

CHEMICAL ANALYSIS TECHNIQUES

Uranium

A 0.5 gram sample contained in a platinum crucible was weighed and ignited at 1000°C. A mixture of hydrofluoric, nitric, and sulfuric acids was added to the cooled sample and evaporated until SO_3 fumes were noticeable. The contents of the crucible were then transferred to a 150 milliliter beaker with the aid of water. Iron was separated from the uranium by the addition of ammonium hydroxide and ammonium carbonate and the precipitate was repeatedly washed with ammonium carbonate. The filtrate and washings were then acidified with nitric acid and heated to boiling. The uranium was precipitated from the cooled solution with ammonium hydroxide, filtered, and ignited to constant weight at 1000°C. The uranium content of the sample was then calculated on the basis of the weight of the U_3O_8 recovered.

Carbon Analysis

In order to ascertain the completeness of reaction in the formation of UC, it is necessary to determine the combined carbon and the free carbon content of a sample. This has been accomplished by determining the total carbon and free carbon contents and calculating the combined carbon from these values.

Total Carbon Analysis

A 0.5 gram sample was weighed into a combustion boat and covered lightly with alumina boat bedding. Ignition was carried out in a standard combustion train at 1150-1200°C. for 25 minutes with oxygen. The carbon dioxide generated was purified by passing it through a Lundel gas purifying tube containing $H_2SO_4 \cdot Cr_2O_3$, a Fleming purifying jar with H_2SO_4, and finally a P_2O_5 tube. The purified CO_2 was absorbed in ascarite and weighed.

Free Carbon Analysis

One gram of the carbide sample was dissolved in 50 milliliters containing 3 volumes of HNO_3 to 5 volumes of water and heated on a sand bath until the carbides were decomposed. The resulting sample was filtered through a Gooch filter containing a previously ignited asbestos pad. The residue was washed with $HCl:H_2O(1:20)$,

then with hot water and dried at 110°C. The graphitic carbon content was determined by the combustion method described above.

Nitrogen Analysis

A one gram sample was weighed on tared aluminum foil and placed in a stainless steel boat containing 25 grams of previously melted potassium hydroxide. The charge was inserted into a furnace equipped with a stainless steel tube and heated to 500-600°C. After 40 minutes of fusion the ammonia produced from the nitrides was flushed by passing argon through the train and scrubbed through a hot 20 percent sodium hydroxide solution. The condensate from this scrub solution was collected in a 50 milliliter boric acid solution and titrated with 0.10N sulfuric acid.

Iron Analysis

The iron content of precipitates described in the Uranium section was determined colorimetrically with thiocyanate.

Determination of Silicon in Uranium Silicide

1. Transfer 0.3 to 0.4 grams of the sample to a 250 milliliter beaker using the plastic vial containing the sample as a weighing bottle.

2. Add 50 milliliters of HNO_3 (1:4) and cover beaker.

3. Heat on hot plate until the reaction is complete and the silica is white. Add more HNO_3 (1:4), if necessary.

4. Wash cover and sides of beaker. Add 25 milliliters of H_2SO_4, HNO_3 solution. Cover with speedy-vap.

Solution: 600 milliliters distilled H_2O
200 milliliters concentrated H_2SO_4
200 milliliters concentrated HNO_3

5. Evaporate to fumes of SO_3.

6. Cool. Add 50 to 75 milliliters of distilled water.

7. Heat to dissolve salts.

8. Filter on #40 Whatman filter paper. Wash with hot wash solution (HCl - 1:99).

9. Ignite in a platinum crucible to constant weight. If ignited silica is not white, fuse in a small amount of Na_2CO_3. Dissolve melt in distilled water, acidify with HCl and add 5 milliliters of H_2SO_4. Cover with a speedy-vap and proceed with step 5 through step 9.

10. Weigh.

11. Add 5 milliliters of HF and two drops concentrated H_2SO_4.

12. Evaporate to dryness on sand bath.

13. Ignite and weigh.

Oxygen

Determined by vacuum fusion by National Research Corporation.

REVIEW OF LITERATURE ON URANIUM NITRIDES

1. The System, U-N

No diagram has been constructed for the uranium nitrogen system. Katz and Rabinowitch[1] have surveyed the work on the system. They report the existence of three compounds: UN, U_2N_3 and UN_2. Between UN and U_2N_3, the system is heterogeneous, consisting of two separate phases, UN and U_2N_3. According to Rundle and co-workers[2], the system remains one phase throughout the region from uranium sesquinitride, U_2N_3, to the dinitride, UN_2. Only the extreme ends of the phase need be considered as distinct compounds.

2. Crystallography

a. Uranium Mononitride

UN is face-centered cubic with a lattice constant a = 4.880Å[2], given by Rundle, and a = 4.8899Å[3] by Kempter and co-workers. X-ray density is 14.31-14.32 grams per cubic centimeter[2], [3]. Both Rundle and Kempter report that there are four uranium atoms in a unit cell and that the structure is of the rock salt type rather than of the zinc sulfide type. It is entirely isomorphous with uranium monocarbide, UC[2]. The monocarbide is also face-centered cubic with a = 4.951Å, according to Rundle, and a = 4.955Å, according to Litz and co-workers[4]. It is also isomorphous with UO and it is likely that UN will exhibit complete solid miscibility with UC and UO[2]. Rundle[5] discusses the bonding mechanism between uranium and nitrogen.

b. Uranium Sesquinitride

U_2N_3 is body-centered cubic, with a = 10.678Å and x-ray density of 11.24 grams per cubic centimeter, according to Rundle[2]. On the other hand, other investigators report that U_2N_3 has a hexagonal lattice with a = 3.70Å and c = 5.80Å.[6]

As the nitrogen-to-uranium ratio is increased from 1.5 to 1.75, the U_2N_3 lattice constant decreases from 10.678Å to 10.580Å; from 1.75 to 2.00, the lattice increases from 10.580Å to 10.62 (2 x 5.31)Å. The decrease is interpreted to mean that there is solubility over the entire range between the distorted-fluorite structure of U_2N_3 and the fluorite structure of UN_2[2].

c. Uranium Dinitride

UN_2 has the fluorite structure with a = 5.31Å[2], and an x-ray density of 11.73[1] grams per cubic centimeter.

3. The Preparation of Uranium Nitrides

In general, the following preparation methods of uranium nitrides are described in the literature and summarized by Katz and Rabinowitch[1]:

a. Reaction of uranium metal (powder or turnings) with nitrogen or ammonia [1], [7], [8], [9].

b. Reaction of UH_3 with nitrogen or ammonia[1].

c. Reaction of UCl_4 or 2 NaCl· UCl_4 with ammonia[1].

d. Reaction of U_3O_8 with magnesium in a nitrogen stream[1].

e. Reaction of uranium metal or its alloys with Mg_3N in vacuum[1].

f. Reaction of UC_2 with nitrogen[1], [10].

Only the reactions of uranium, UH_3, or UCl_4 with nitrogen or ammonia are considered to produce nitride not contaminated by other solids, which are difficult to remove. If uranium nitride is prepared by the action of nitrogen or ammonia on uranium or uranium hydride at temperatures up to 1300°C., the reaction does not stop or slow down at the composition UN, but proceeds to U_2N_3 and beyond.

Of the uranium nitrides, UN is the only compound stable at high temperatures[8]. Therefore, UN is prepared by decomposition of the higher nitrides in vacuum above 1300°C.

The preparation of uranium nitrides by nitriding mixtures of uranium oxide (UO_2 or U_3O_8) or ammonium diuranate, $(NH_4)_2U_2O_7$, and carbon is not mentioned in the literature.

In the literature the preparation of uranium carbide from the oxides (UO_2 or U_3O_8) is described. Litz and co-workers[4] state that UC is readily prepared by heating U_3O_8 with the stoichiometric

amount of graphite to 1800°C.; higher temperatures yield UC_2, according to the reactions:

$$U_3O_8 + 11C \xrightarrow{1800^\circ C.} 3\ UC + 8\ CO$$

$$U_3O_8 + 14C \xrightarrow{2400^\circ C.} 3\ UC_2 + 8\ CO$$

Austin and Gerds[10] studied the ternary system uranium-nitrogen-carbon at 1800°C. under vacuum and under nitrogen at atmospheric pressure. There is complete solid solubility between UN and UC, and essentially no solid solubility of nitrogen in UC_2 or U_2C_3 or of carbon in U_2N_3. At 1800°C., the two-phase field, U(C, N) and UC_2, and the three-phase field, U(C, N), UC_2 and C, exist in vacuum or argon. They investigated also the reaction of uranium carbides with nitrogen at atmospheric pressure from 1000°C. to 2000°C. Up to 1800°C., uranium nitrides and free carbon are formed, but at 2000°C., the uranium carbides UC_2 + U(C, N) become more stable. At 1 atmosphere of nitrogen, U_2N_3 is the stable phase up to 1550°C., and U(N, C) solid solution is stable at 1800°C.

4. The Physical and Chemical Properties of Uranium Nitrides

Uranium mononitride is described as light-gray powder with a melting point about 2650°C. plus or minus 100°C.[8], [9]. It is quite stable in vacuum at 1700°C.

Small uranium nitride crucibles[8], pressed at between 50,000 and 60,000 pounds per square inch and fired to between 2000°C. and 2100°C., had a density of approximately 12.0 grams per cubic centimeter.

Tripler and co-workers[9] obtained densities between 83 and 90 percent of theoretical during vacuum sintering of UN at about 1850°C. They report a Knoop microhardness for sintered UN, using a 100 gram load, of 455.

Thermodynamic estimates made at Battelle[11] predict reaction of UN with oxygen, H_2O, and steam, and no reaction with hydrogen. A porous compact of UN reacted with acids, and with boiling water, but did not react with 1N NaOH.

In a finely-divided state, uranium nitrides are reported as being pyrophoric[1].

5. Literature References on Uranium Nitrides

(1) J. J. Katz and Eugene Rabinowitch, "The Chemistry of Uranium," Part I, McGraw-Hill Book Company, Inc., New York (1951) 232-241.

(2) R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, The Structures of the Carbides, Nitrides and Oxides of Uranium, J. Am. Chem. Soc., 70, 99-105 (1948).

(3) C. P. Kempter, J. C. McGuire, and M. R. Nadler, Uranium Mononitride, Anal. Chem., 31, No. 1, 156-157 (1959).

(4) L. Litz, A. B. Garrett, and F. C. Croxton, Preparation and Structure of the Carbides of Uranium, J. Am. Chem. Soc., 70, 1718 (1948).

(5) R. E. Rundle, A New Interpretation of Interstitial Compounds: Metallic Carbides, Nitrides, and Oxides of Composition MX, Acta Cryst. 1, 180-187 (1948).

(6) H. A. Saller and F. A. Rough, Compilation of U.S. and U.K. Uranium and Thorium Constitutional Diagrams, Battelle Report BMI-1000 (June 1955).

(7) M. W. Mallet and A. F. Gerds, Reaction of Nitrogen with Uranium, J. Electrochem. Soc., 102, 292-296 (1955).

(8) P. Chiotti, Experimental Refractory Bodies of High-Melting Nitrides, Carbides, and Uranium Dioxide, J. Am. Chem. Soc., 35, No. 5, pp. 123-130, 1952.

(9) A. B. Tripler, J. M. Snyder, and W. H. Duckworth, Further Studies of Sintered Refractory Uranium Compounds, Battelle Report No. BMI-1313 (January 1959).

(10) A. E. Austin and A. F. Gerds, The Uranium-Nitrogen-Carbon System, Battelle Report No. BMI-1272 (June 1958).

(11) M. J. Snyder, G. B. Engle, and L. D. Loch, Properties of Some Refractory Fuel Compounds, U. S. Atomic Energy Commission TID-7530 (Pt. 1), 141-3 (1957).

REVIEW OF THE LITERATURE ON URANIUM SILICIDES

1. The System, U-Si

The phase diagram for the uranium-silicon system, as published by Katz and Rabinowitch[1], contained five intermediate compounds. This phase diagram was based on studies performed at M.I.T. by Kaufmann, Cullity, Bitsianes, Gordon, Cohen and Bastian. The phases reported originally were $U_{10}Si$, U_5Si_3, USi, U_2Si_3, USi_2, and USi_3.

In 1949 Zachariasen[2] reported that the compound $U_{10}Si_3$ was actually U_3Si, the compound U_5Si_3 was U_3Si_2, and finally, that the compound U_2Si_3 was actually a modification of USi_2.

Later in 1957, Kaufmann, Cullity, and Bitsianes[3] published the phase diagram shown in Figure 7 of Appendix 4, which contains the compounds U_3Si (epsilon phase), U_3Si_2, USi, U_2Si_3, USi_2, and USi_3. They claimed that the so-called epsilon phase did not fall exactly on the composition U_3Si. Furthermore, they stated that the compound, alpha USi_2, did not transform at high temperatures to the beta form, and hence they show the compound U_2Si_3 in its place.

They report that the compound U_3Si forms at 930°C. through a peritectic reaction between U_3Si_2 and gamma uranium-silicon solid solution. A eutectic exists between gamma uranium and U_3Si_2 at 9 atom percent silicon and a temperature of 985°C. The next compound found is U_3Si_2, melting congruently at 1665°C. The next compound found is USi, which has an incongruent melting point of 1575°C. Following this is U_2Si_3, again melting incongruently at 1610°C. USi_2 is reported to melt congruently at about 1700°C. Finally, the compound USi_3 is shown to have an incongruent melting point at 1510°C.

Two additional eutectics are shown, the first located at 1570°C. between U_3Si_2 and USi, while the second is at 87 atomic percent silicon between USi_3 and silicon at 1315°C. Kaufmann et al.[3] noted that there was appreciable solid solubility of silicon in uranium.

2. Crystallography

The crystal structure of uranium disilicide was reported by Brauer and Haag[4] to be face-centered cubic, with a lattice para-

meter of a_o = 4.053 Å. However, Zachariasen[2] reports this phase (alpha USi_2) to be body-centered tetragonal type. The lattice parameters of this compound, along with those of U_3Si, U_3Si_2, USi, beta USi_2 and USi_3, as reported by Zachariasen, are shown in the following table:

Crystallographic Data and Density of Uranium Silicides

Compound	Structure	Lattice Parameters	Theoretical X-Ray Density, g/cc.
U_3Si	Body-centered Tetragonal	a = 6.067Å c = 8.679Å	15.58
U_3Si_2	Tetragonal	a = 7.3151 c = 3.8925	12.20
USi	Orthorhombic	a = 5.65Å b = 7.65 c = 3.70	10.40
Beta USi_2)* or U_2Si_3)	Hexagonal	a = 3.85 c = 4.06	9.25
USi_2	Body-centered Tetragonal	a = 3.97 c = 13.71	8.98
USi_3	Cubic	a = 4.03	8.15

*Beta USi_2 according to Zachariasen, and U_2Si_3 according to Kaufmann.

3. Synthesis and Fabrication

The uranium silicides have been prepared by many different methods; Defacqz[5] reported the formation of uranium disilicide in 1908 by an aluminothermic reaction. Later, Brauer and Haag[4] succeeded in preparing the disilicide from the elements in a menstruum of molten aluminum. The other attempts at preparation have been centered around a direct combination of the two elements. Kaufmann, Cullity and Bitsianes[3] prepared uranium silicon alloys, as described by Gordon and Kaufmann[6], by melting the elements

in beryllia or beryllia-lined crucibles heated by high frequency techniques in either vacuum or an atmosphere of argon. Resistance-heated melting furnaces were found unsuccessful because of the lack of eddy current stirring. Epsilon alloys (U_3Si) were prepared by S. Isserow[7] by melting in zirconia-washed graphite crucibles in induction-heated vacuum furnaces. Loch, Engle, Snyder and Duckworth[8] prepared uranium silicon alloys by melting in an electric arc furnace.

The fabrication of uranium silicides into test specimens has been largely carried out by casting, following either arc melting[12] or induction-heated melting[7]. The epsilon phase has been extruded and coextruded successfully at temperatures of 750-850°C.[10], [13]

U_3Si_2, USi, USi_2, and USi_3 have been sintered to densities of 81.7 to 99.4 percent theoretical in vacuum[12]. Loch and coworkers[8] report sintering of uranium silicides in an argon atmosphere.

4. Chemical and Physical Properties

Of the various uranium silicide compounds U_3Si (the epsilon phase) has received by far the most attention because of its high uranium density (14.98 grams per cubic centimeter) and its excellent corrosion resistance in high temperature water. Isserow[7] deals extensively with the epsilon phase (U_3Si) and states that the pure compound is formed from the as-cast alloy, U + U_3Si_2, only after annealing at 800°C. for one week. He reports that the corrosion resistance is dependent upon the absence of other phases (U, U_3Si_2, etc.) in the alloy and found weight losses of 50 milligrams per square centimeter per month in 500°F. water. He found an initial corrosion rate of 1000-1500 milligrams per square centimeter per month in 650°F. water. However, samples subjected to 750°F. steam for 48 hours experienced extensive corrosion with substantial portions of the sample being converted to sludge. Samples not completely converted to the epsilon alloy have less corrosion resistance.

Isserow[7] briefly studied the corrosion of the epsilon phase in molten lead. Here it was found that samples held at 350 to 425°C. did not form intermediate layers. However, at 500°C. or above, an intermediate layer of UPb_3 was formed.

Loch et al.[8] indicate that there is no reaction of U_3Si and alpha USi_2 with boiling water and they report weight losses of 1 to 2 milligrams per square centimeter per hour in 650°F. water.

While Katz and Rabinowitch[1] report that the disilicide is attacked by hydrofluoric acid, it is resistant to mineral acids, including aqua regia. Loch and coworkers show that U_3Si, and alpha USi_2 react with concentrated HCl, HNO_3 and H_2SO_4, but that no reaction occurs with 1N NaOH.

It is reported by Katz and Rabinowitch[1] that the disilicide is converted to the silicate and uranate at red heat by heating with molten alkali and alkali carbonate. They also indicate that the disilicide reacts with chlorine at 500°C.

Loch et al.[8] state that U_3Si, and beta USi_2 show a slight weight gain (0.08-0.62 percent) in hydrogen at 500°C. for one hour.

None of the uranium silicides are reported to exhibit much oxidation resistance. Katz and Rabinowitch[1] state that the disilicide burns in air at 800°C. The following table shows the results of Loch et al.[8]:

Compound	Silicon Content, w/o	Weight Gain in 7-1/2 Hours at 400°C., %
U_3Si	3.8	19.6 (disintegrated)
U_3Si_2	7.25	18.5 (disintegrated)
		1.4 (with 3-5% iron)
USi	10.5	16.5 (disintegrated)
Beta USi_2	19.0	0.19 (with 1 w/o tungsten)
USi_3	26.0	0.07 (with 4 w/o tungsten)

Koenig[12] reports that the oxidation of cast U_3Si_2 is quite rapid at 315°C., with cracking occurring after four hours and complete disintegration after 16 hours. He indicates that U_3Si_2 is stable at 100°C. but undergoes slight oxidation at 200°C.

Snyder and Duckworth[9] studied the initial oxidation of USi_2, USi_3, and U_3Si_2. Up to about 400°C., protective films were found and rate of oxidation followed a parabolic law. However, metallic uranium, and USi form non-protective oxide layers at these temperatures. These tests were of a shorter duration than that reported by Koenig[12].

The reaction of uranium silicides with nitrogen was studied by Snyder and Duckworth[9]. They indicate that while protective surface films were built up on all of the silicides, at temperatures of 400 to 700°C., the reaction rates were higher than those of nitrogen and uranium. Again, the reaction follows a parabolic law.

Isserow[7] states that tensile tests on an extruded and machined U_3Si rod gave 100,000 pounds per square inch as an ultimate strength and a proportional limit of about 60,000 pounds per square inch. The values obtained after annealing were about 60 percent of these values. A total elongation of approximately one percent was experienced. The elastic modulus is reported to be near 22.5×10^6 pounds per square inch. The coefficient of linear expansion is reported[7] from room temperature to the temperatures indicated below:

Temperature, °C.	300	600	800
Coefficient of Expansion, 10^6 psi.	12	14	16

The electrical resistivity of the epsilon phase is reported[7] to be 55 microhm-centimeters at room temperature.

The thermal conductivity of the epsilon phase (U_3Si) is reported by Bitsianes[13] as shown in the following table:

	Thermal Conductivity, Cal/cm/cm^2/sec/°C.	
Temp., °C.	19 atomic % Silicon	23 atomic % Silicon
25	-	0.036
30	0.040	0.037
40	0.042	0.039
50	0.044	0.041
60	0.045	0.042

R. W. Nichols[19] reports the thermal conductivity of U_3Si_2 to be 0.035 cal/cm/cm^2/sec/°C. at 65°C.

Tensile and compression testing stress-strain data is summarized by Goldman[15] This work was performed on the epsilon alloys. As an example of the results for a 23 atom percent silicon alloy, the room temperature strain in tension at 37,000 pounds per square inch was 0.23 percent.

The properties of the epsilon alloys are dependent upon the amount of U_3Si formed. Koenig and Webb[10] indicate that U_3Si has a Vickers hardness of 240 while the "as-cast" alloy has a hardness of 530 Vickers hardness number. The density increases with increasing U_3Si content and the resistivity decreases. The

resistivity of U_3Si increases with temperature. The magnitude of the resistivity changes are shown in the following table:

Electrical Resistivity of U-3.8 w/o Si as a Function of Epsilon Phase Content and Temperature

Treatment	Epsilon Phase, %	Resistivity Microhm-cm, at Temperature, °C. -200	25	200	400
Heated at 800°C. for several days in vacuum	95	25.97	57.67	65.36	70.58
As-Cast	0	42.51	63.88	78.42	84.14

Data on the thermal expansion of three uranium silicides, U_3Si, U_3Si_2, and USi_2, are shown in the table below, as reported by Loch and coworkers[8]:

Temperature Range, °C.	Mean Coefficient of Linear Thermal Expansion, cm/cm/°C. x 10^{-6} U_3Si	U_3Si_2	USi_3 (+ 4 w/o tungsten)
20-200	13.0	15.5	13.4
20-300	13.4	15.3	13.6
20-400	14.2	15.2	14.3
20-500	14.9	15.3	14.6
20-600	15.8	15.2	14.9
20-700	16.8	15.1	15.4
20-750	17.5	-	-
20-800	-	15.0	15.7
20-900	-	14.7	16.1
20-950	-	14.6	16.3

The following tables, taken from a report by Snyder and Duckworth[9], show the thermal expansion coefficients, microhardness, and specific heats of USi_2, USi_3, and U_3Si.

Temp. °C. Range	Mean Linear Thermal Expansion Coefficient x 10^{-6}/°C.					
	USi		USi_2		USi_3	
	Heating	Cooling	Heating	Cooling	Heating	Cooling
20-100	20.0	18.8	15.9	15.1	15.5	15.5
20-200	18.8	18.1	15.6	14.9	15.3	15.6
20-300	17.8	18.2	15.5	15.8	15.4	16.3
20-400	17.4	17.9	15.6	15.8	15.7	16.7
20-500	16.9	17.7	15.5	15.9	15.8	17.1
20-600	16.4	17.7	15.5	16.3	16.6	17.8
20-700	16.1	17.6	15.7	16.6	15.3	18.4
20-800	15.9	17.6	16.2	16.7	15.1	18.8
20-900	15.8	17.4	16.8	16.7	15.0	18.9
20-950	15.7	17.3	16.9	16.7	14.9	19.1

Micro Hardness of Uranium Silicides

Compound	Average Knoop Hardness	
	25 g. load	100 g. load
U_3Si_2	-	796
USi	645	745
USi_2	745	700
USi_3	485	445

Specific Heats of Uranium Silicides

Temp. °C.	Specific Heat, cal/g/°C.		
	USi_2	USi_3	U_3Si
0	0.064	0.077	0.043
50	0.060	0.073	0.033
100	0.064	0.073	0.033
150	0.071	0.077	0.037
200	0.075	0.081	0.042
250	0.070	0.083	0.043
300	0.051	0.083	0.034

The silicide, U_3Si, has undergone irradiation testing[11], [16] and some swelling was experienced, varying from a small amount at burn-ups of 600 megawatt days per ton of uranium to 7 percent at a burn-up of 1600 megawatt days per ton[11]. It was suggested that the swelling was due to a decomposition of the epsilon phase or a disordering effect, resulting in a volume change. Accompanying this is a hardness increase, embrittlement, increase in electrical resistivity, and a change of the normally positive temperature, coefficient of electrical resistivity to negative.

4. Literature References on Uranium Silicides

(1) J. J. Katz, and E. Rabinowitch, "The Chemistry of Uranium - Part I, The Element, Its Binary and Related Compounds," McGraw-Hill Book Company, Inc., New York (1951), pp. 226-229.

(2) W. H. Zachariasen, Crystal Chemical Studies of the 5f - Series of Elements, Acta Crystallographica, 2, 94 (1949).

(3) A. Kaufmann, B. Cullity and G. Bitsianes, Uranium Silicon Alloys, Journal of Metals, 9, Section 2, 23 (1957).

(4) G. Brauer and H. Haag, The Crystal Structure of Uranium Silicide, Z. Anorg. Chem., 259, 197-200 (1949).

(5) E. Defacqz, Compt. rend., 147, 1050 (1908).

(6) P. Gordon and A. R. Kaufmann, The Alloy Systems Uranium-Aluminum and Uranium Iron, Journal of Metals, 188, 182 (1950).

(7) S. Isserow, The Uranium-Silicon Epsilon Phase, Nuclear Metals, Inc., NMI-1145 (April 1956).

(8) L. D. Loch, G. B. Engle, M. J. Snyder and W. H. Duckworth, Survey of Refractory Uranium Compounds, Battelle Memorial Institute, BMI-1124 (August 1956).

(9) M. J. Snyder and W. H. Duckworth, Properties of Some Refractory Uranium Compounds, Battelle Memorial Institute, BMI-1223 (September 1957).

(10) N. R. Koenig and B. A. Webb, Properties of Ceramic and Cermet Fuels for Sodium Graphite Reactors, Atomics International Division, North American Aviation, Inc., NAA-SR-3880 (June 1960) OTS.

(11) L. M. Howe, Irradiation Behavior of Enriched U_3Si Elements Sheathed in Zircaloy, Atomic Energy of Canada Ltd., Chalk River, Ont., CR Met-904.

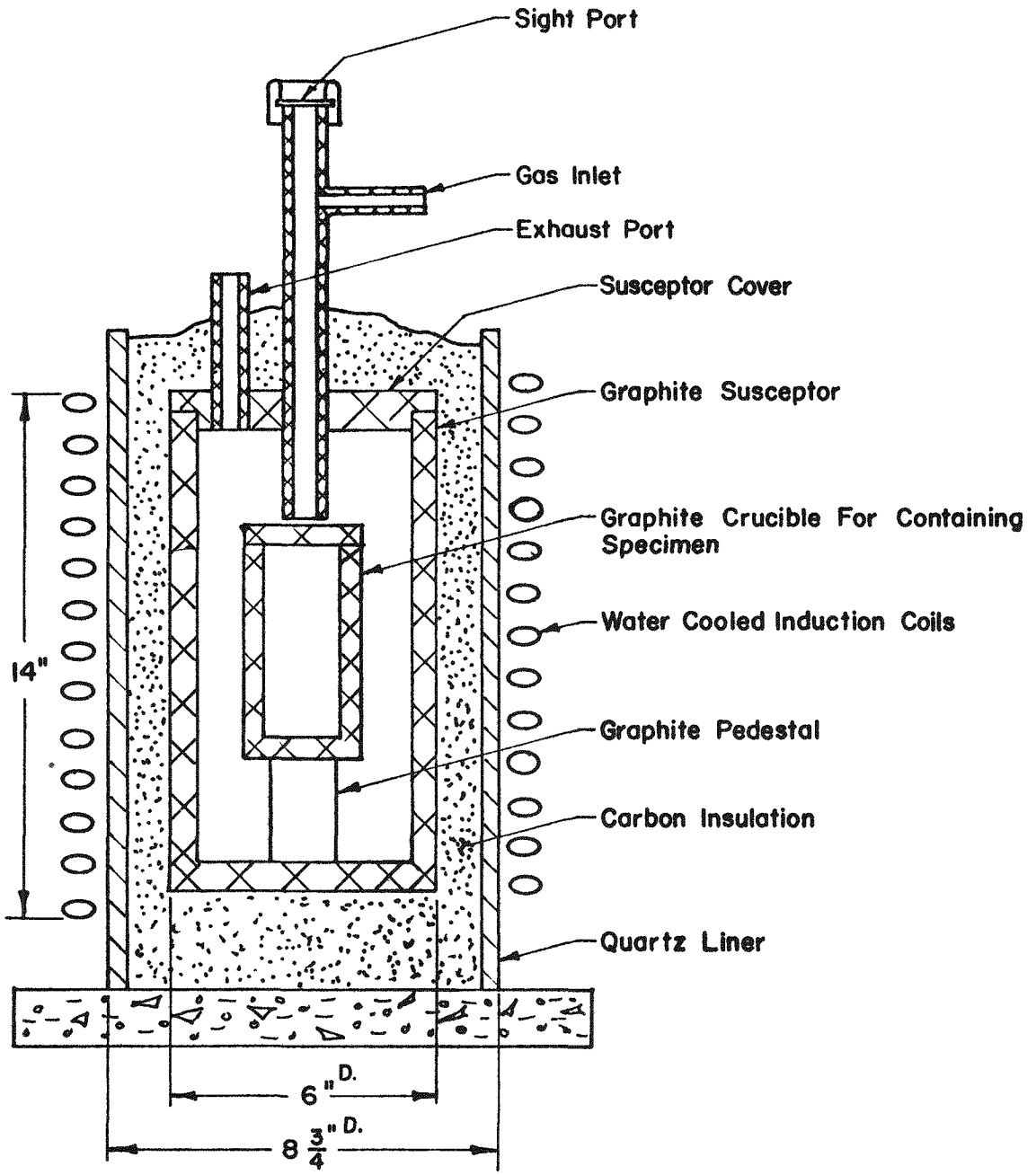
(12) N. R. Koenig, U_3Si_2 Fuel Evaluation, Pt. I, Oxidation Characteristics, Atomics International Division, North American Aviation, Inc., NAA-SR-Memo-5199, (April 1960).

(13) G. Bitsianes, Alloys of Uranium and Silicon - II The Epsilon Phase, CT 3309 (June 1945).

(14) R. W. Nichols, Ceramic Fuels - Properties and Technology, Nuclear Engineering 3, 327 (Aug. 1958).

(15) K. M. Goldman, Preliminary Literature Survey - Uranium Silicon Alloys, WAPD-FE-434 (August 1954) OTS.

(16) M. L. Bleiberg and L. J. Jones, The Effects of Pile-Irradiation on U_3Si, Nuclear Engineering and Science Conference (Chicago, March 1958), Preprint 18 - Session VIII.



SKETCH OF ATMOSPHERE INDUCTION FURNACE

FIG. 1

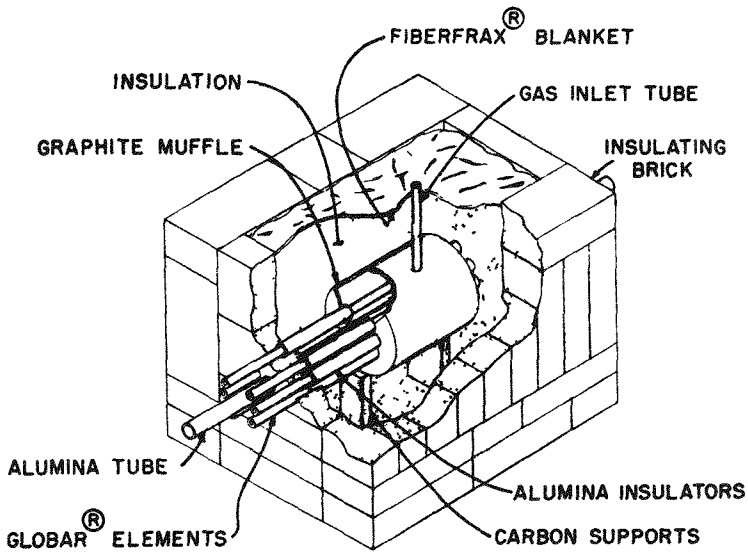


Figure 2 - Alumina Tube Muffle Furnace with Silicon Carbide Heating Elements for Temperatures to 1800°C.

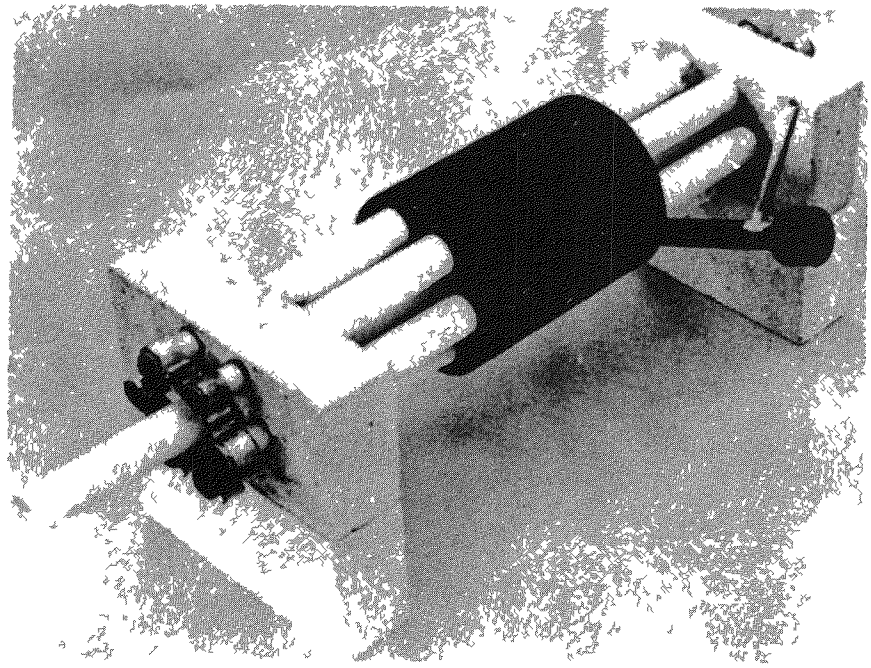
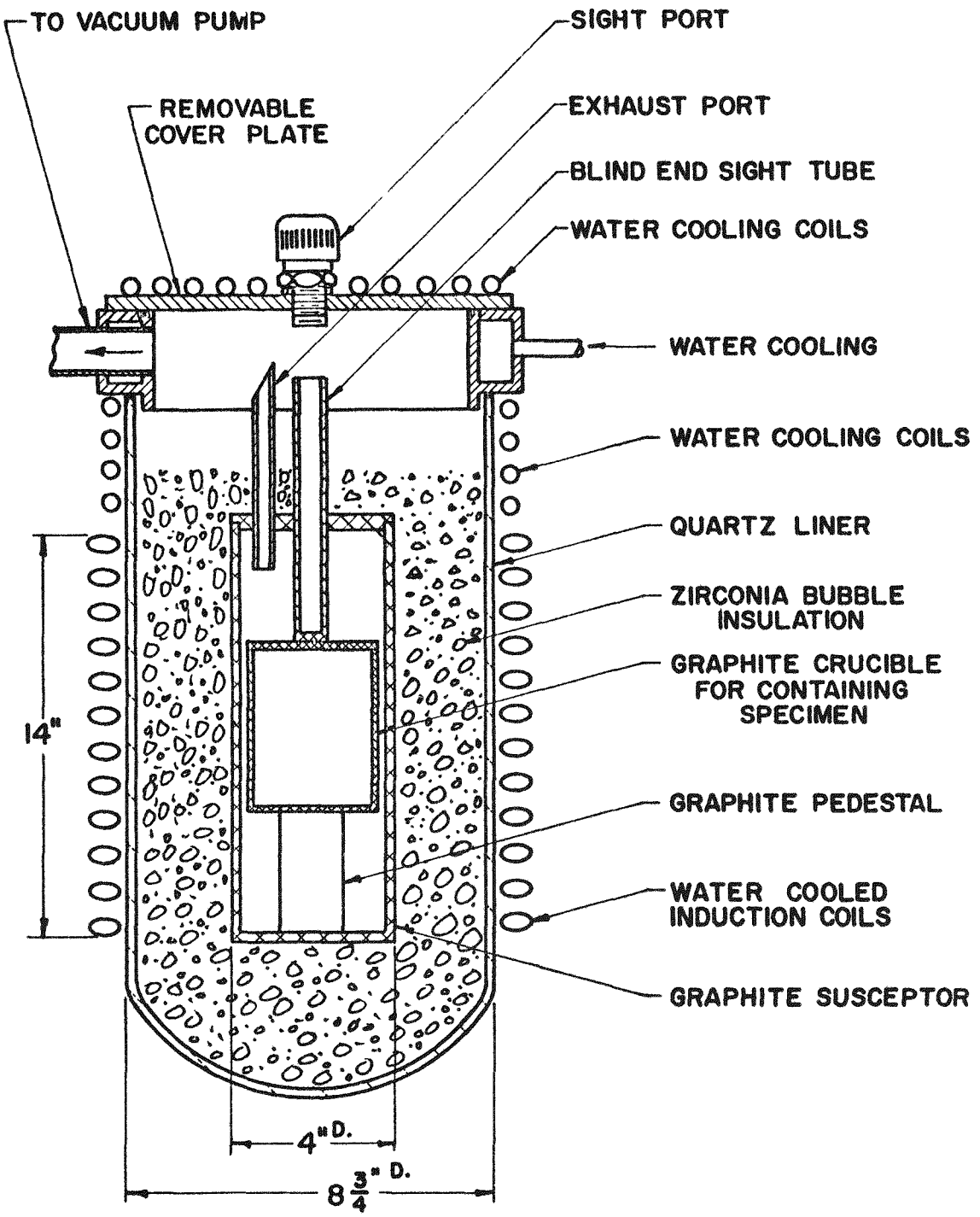
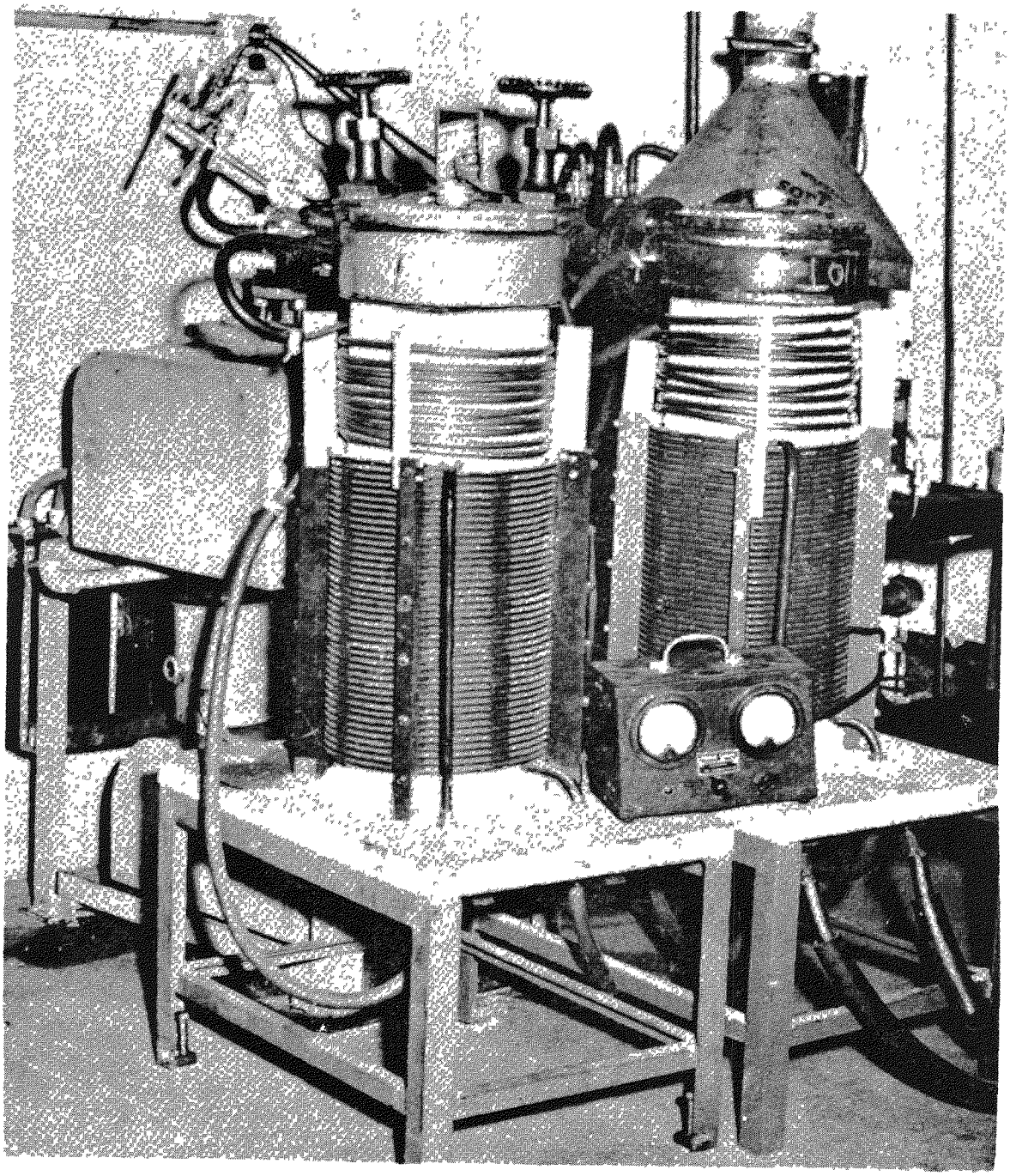


Figure 3 - Detail of Heating Chamber for Furnace Shown in Figure 2.



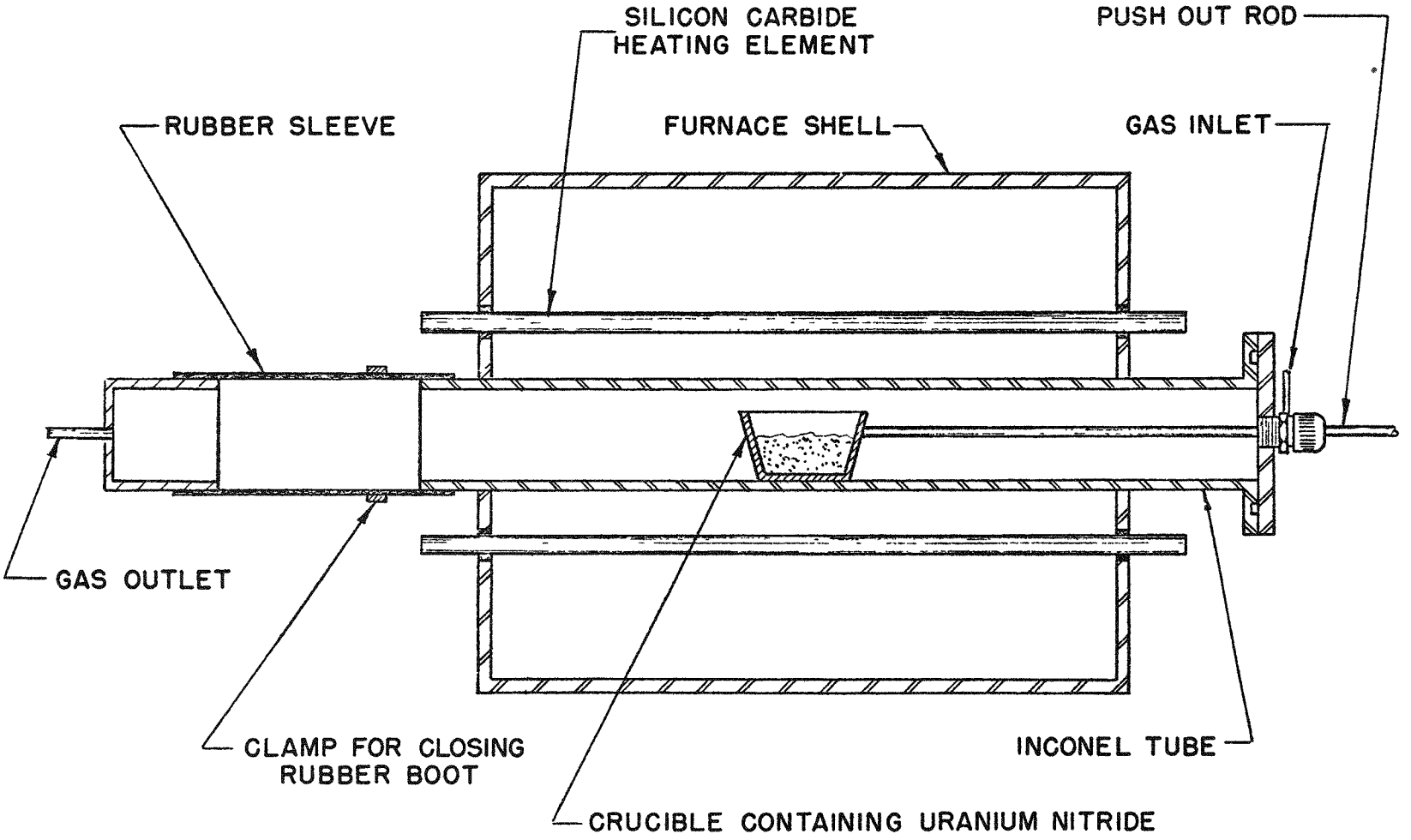
SKETCH OF VACUUM INDUCTION FURNACE

FIG. 4



VACUUM INDUCTION FURNACE

Figure 5



NITRIDING FURNACE

FIGURE 6

THE URANIUM-SILICON SYSTEM

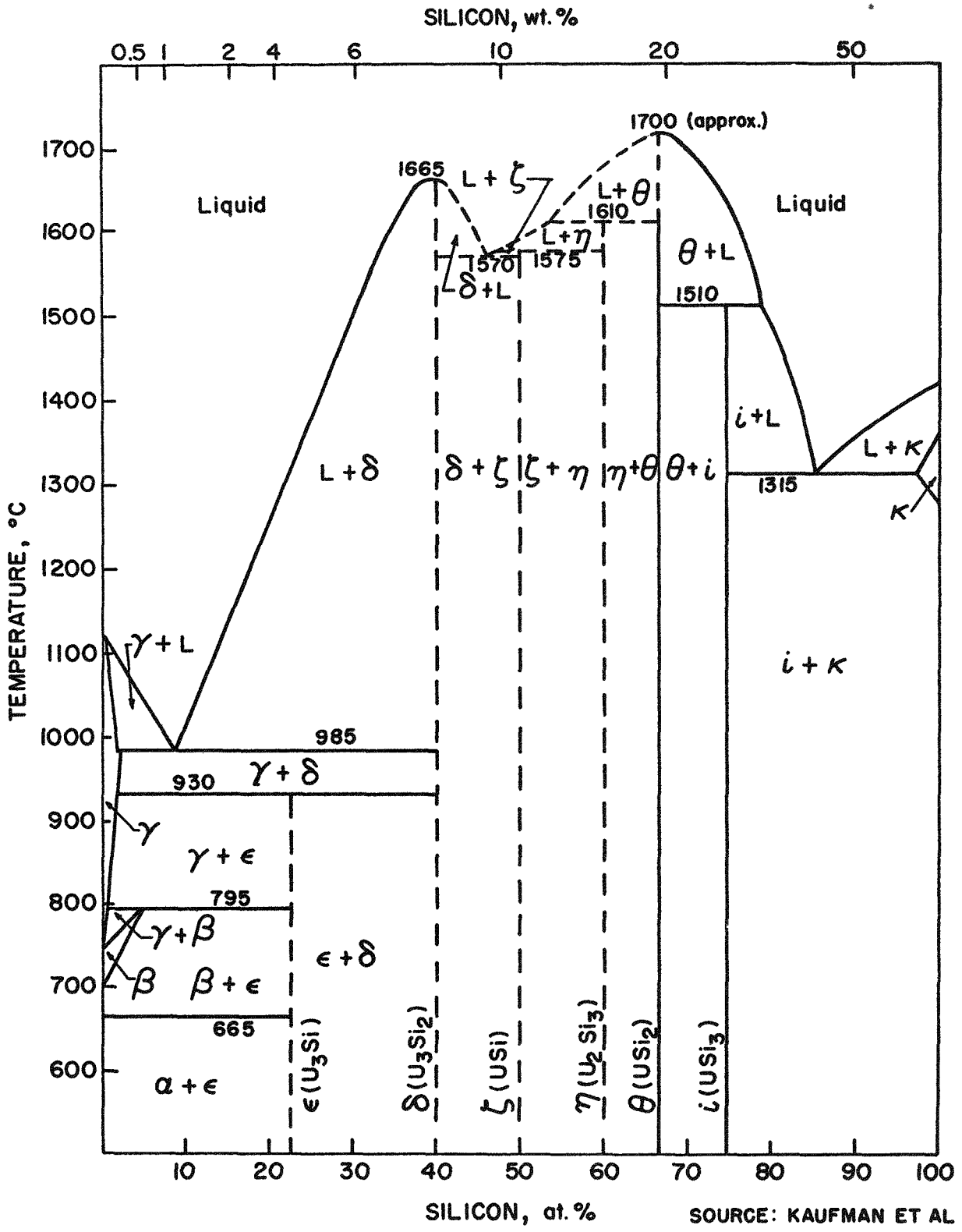
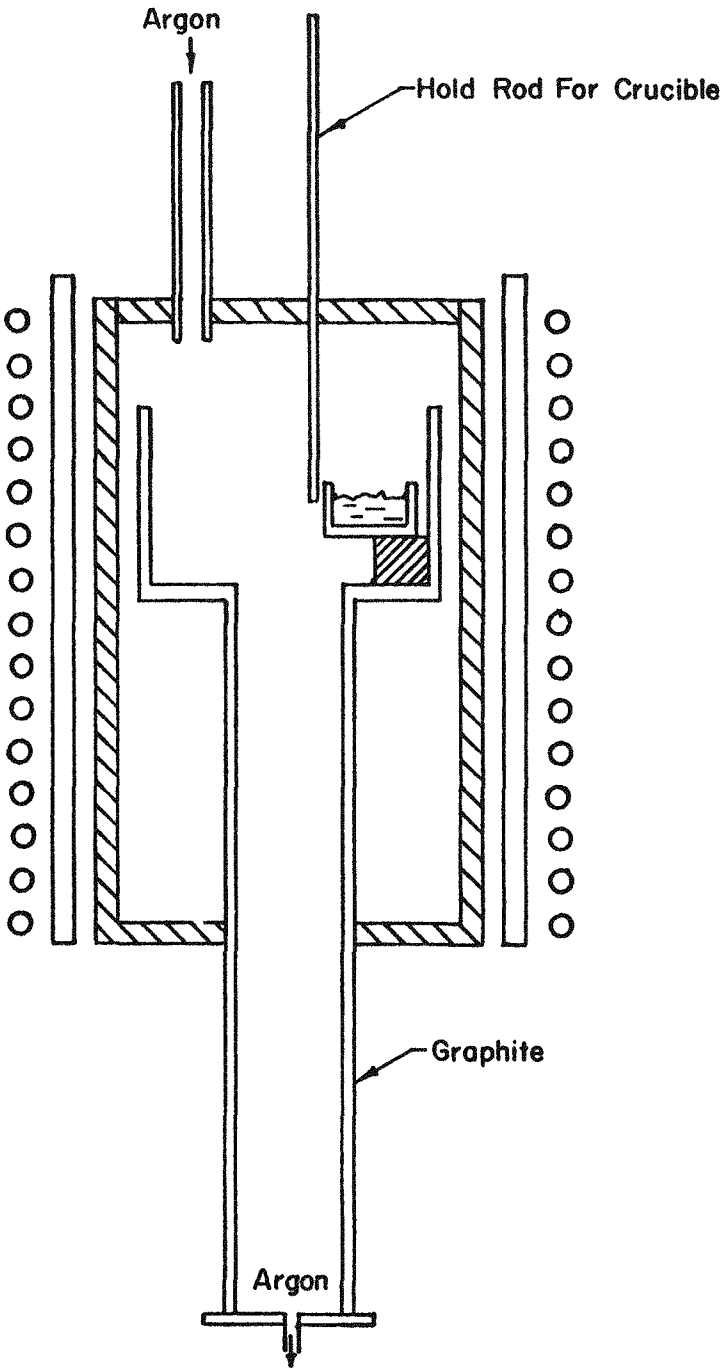


FIGURE 7



QUENCH FURNACE

Fig. 8

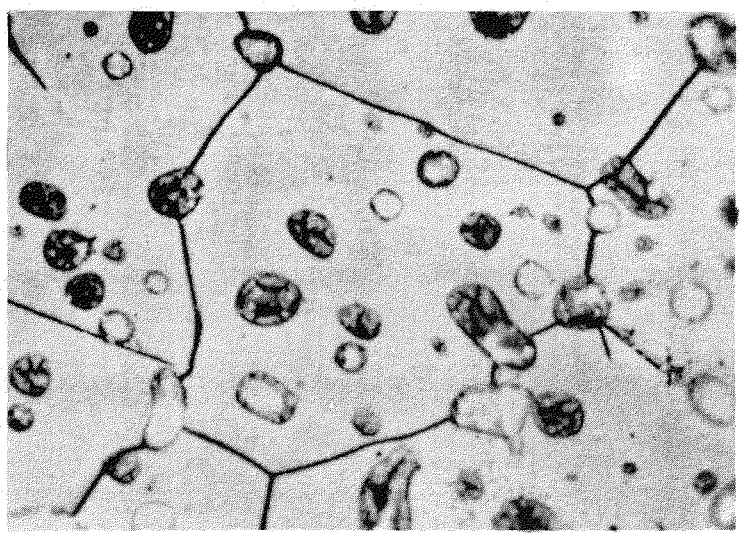


Figure 9a - Single Phase UC - 1000X - Nitric Acid-Acetic Acid-Water Etch. The dots are voids, some of which contain polishing powder.

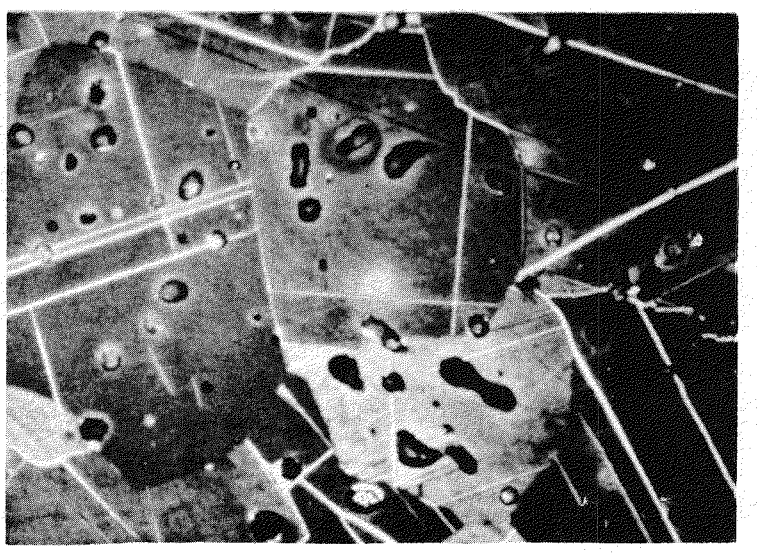


Figure 9b - UC Plus Trace of UC_2 - 1000X - Nitric Acid-Acetic Acid-Water Etch.

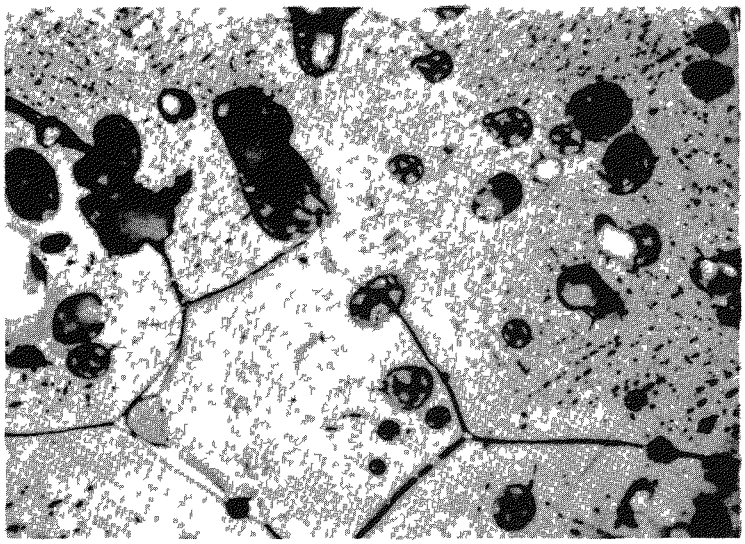


Figure 10a - UC With Small Amounts of Metal at the Grain Boundaries - 1000X - Nitric Acid-Acetic Acid-Water Etch.

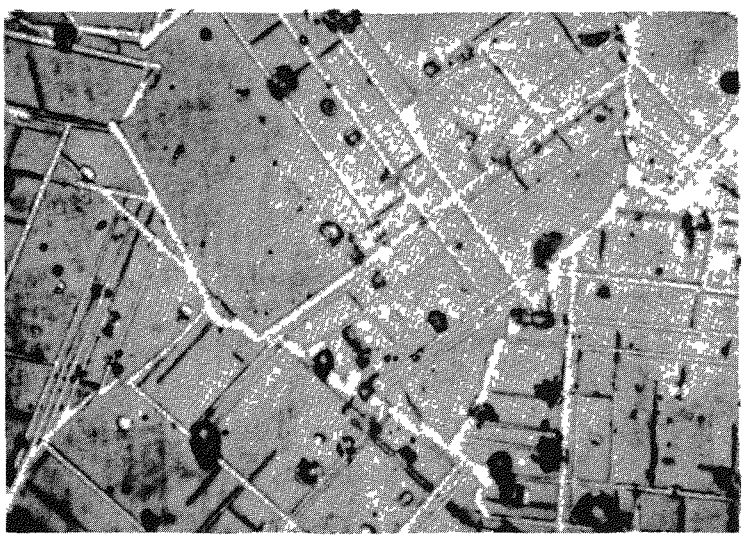
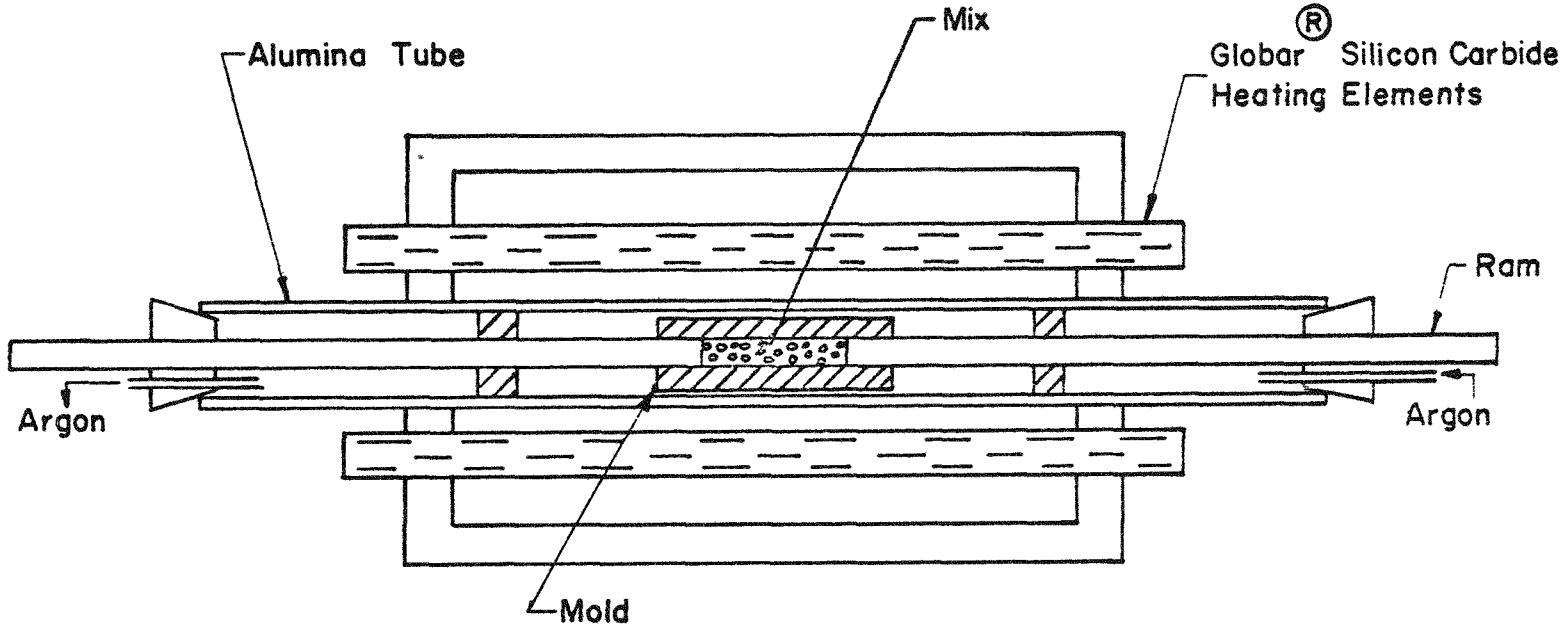


Figure 10b - UC Plus Small Amount of UC_2. Traces of oxide appear at some of the grain boundaries - 1000X - Nitric Acid-Acetic Acid-Water Etch.



HOT-PRESSING FURNACE

Fig. 11

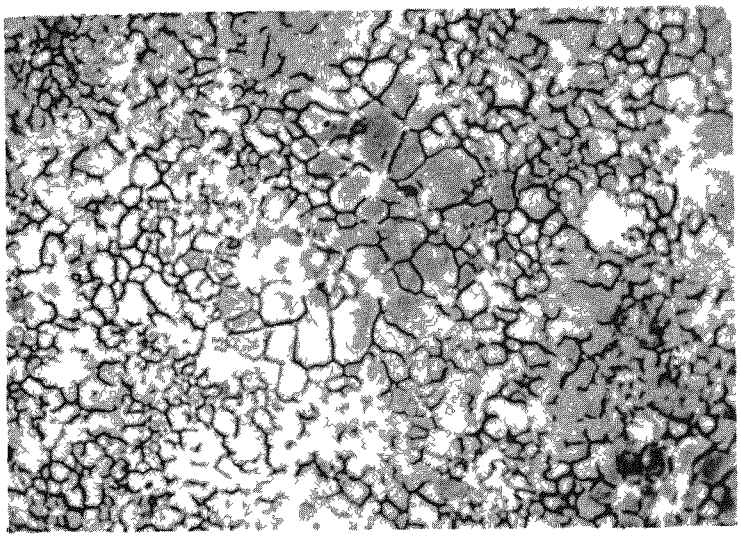


Figure 12 - UC Prepared by Reaction Hot Pressing U + C. The white phase is metal. 1000X - Nitric Acid-Acetic Acid-Water Etch.

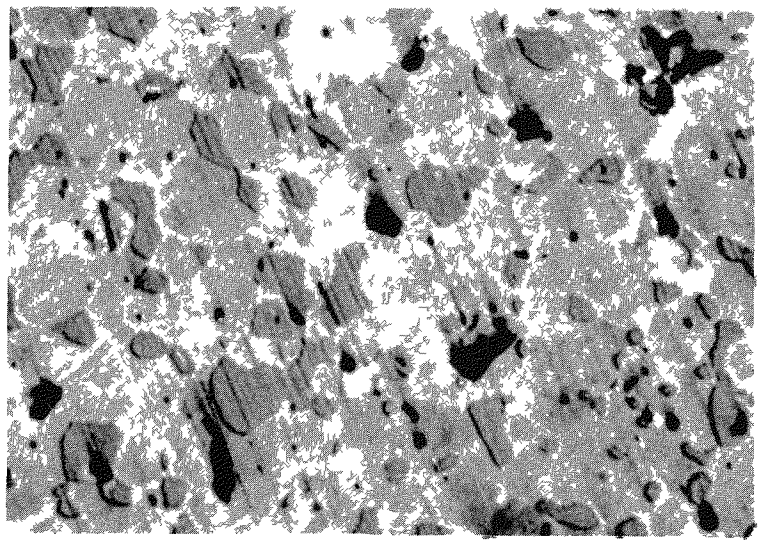


Figure 13 - Sintered UN Containing a White Metal Phase. The black areas are voids. 1000X - Nitric Acid-Acetic Acid-Water Etch.

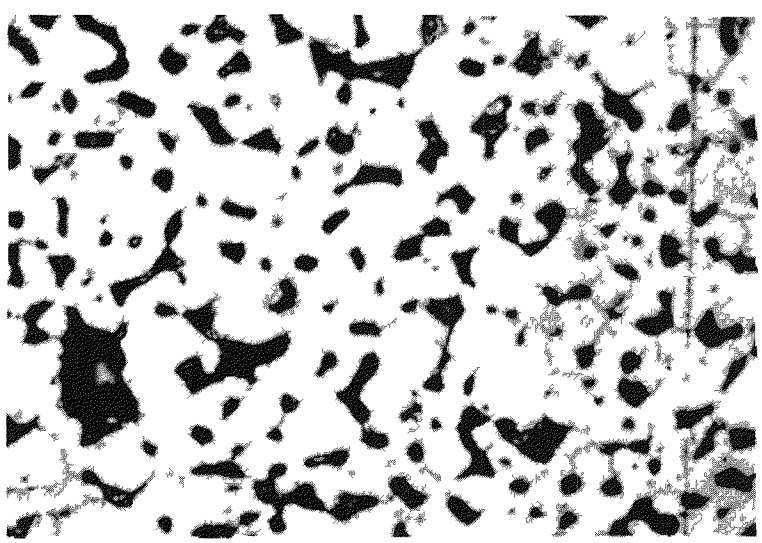


Figure 14 - Sintered Single Phase UN. The dark areas are voids. 1000X - Nitric Acid-Acetic Acid-Water Etch.

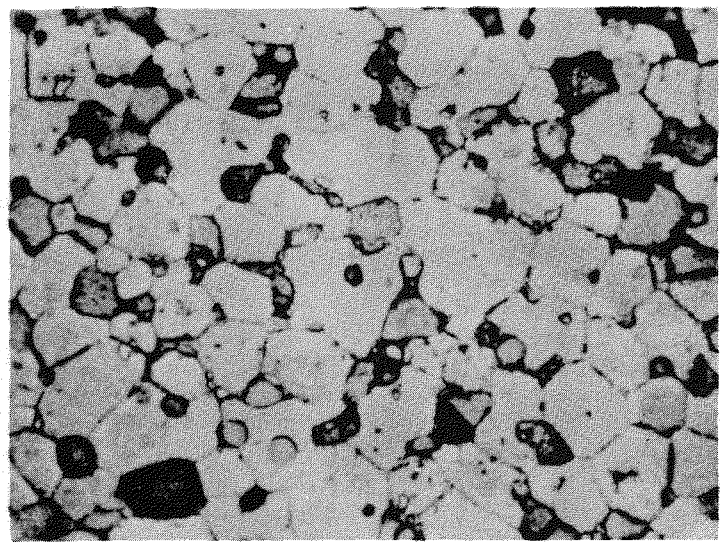


Figure 15 - Sintered UN With a Deficiency of Nitrogen. The light gray phase is UN; the dark gray material may be a second nitride phase; the black areas are voids. 1000X - Nitric Acid-Acetic Acid-Water Etch.

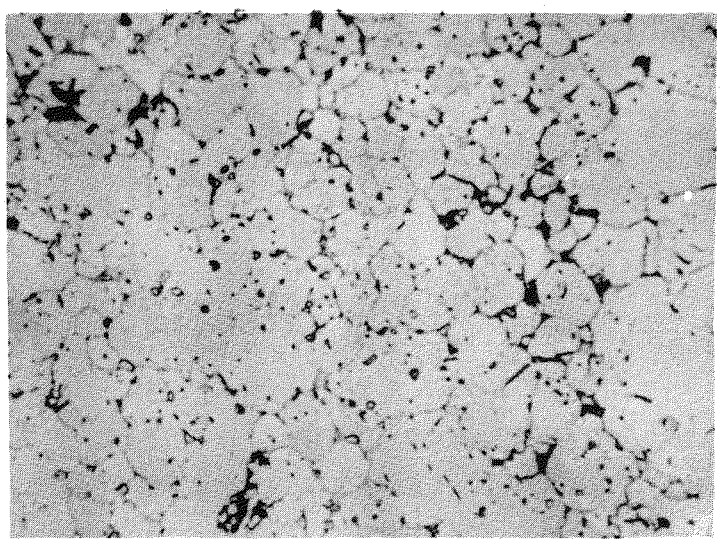


Figure 16 - High Density, Essentially Single Phase U_3Si_2. 1000X - Nitric Acid-Acetic Acid-Water Etch.

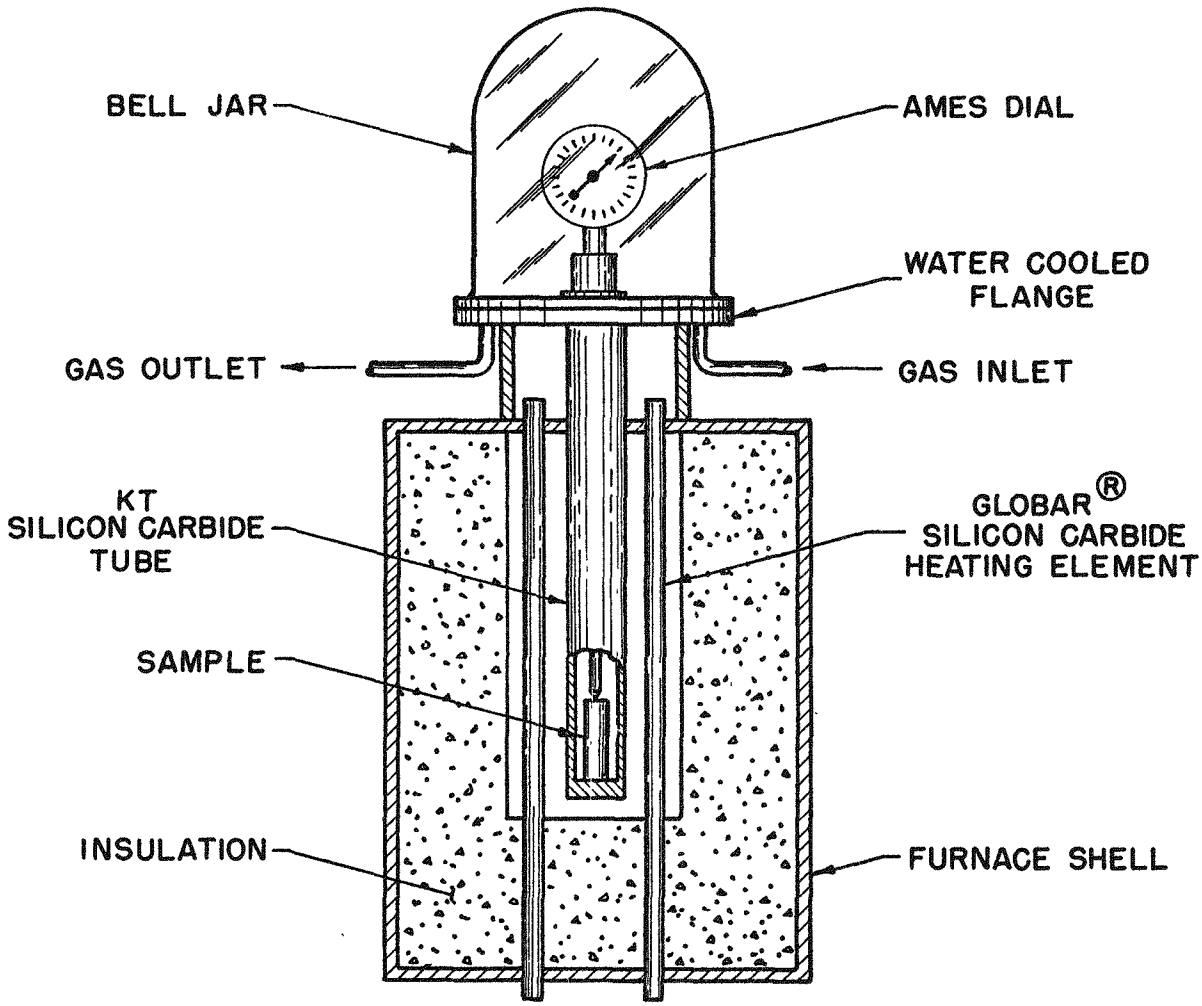
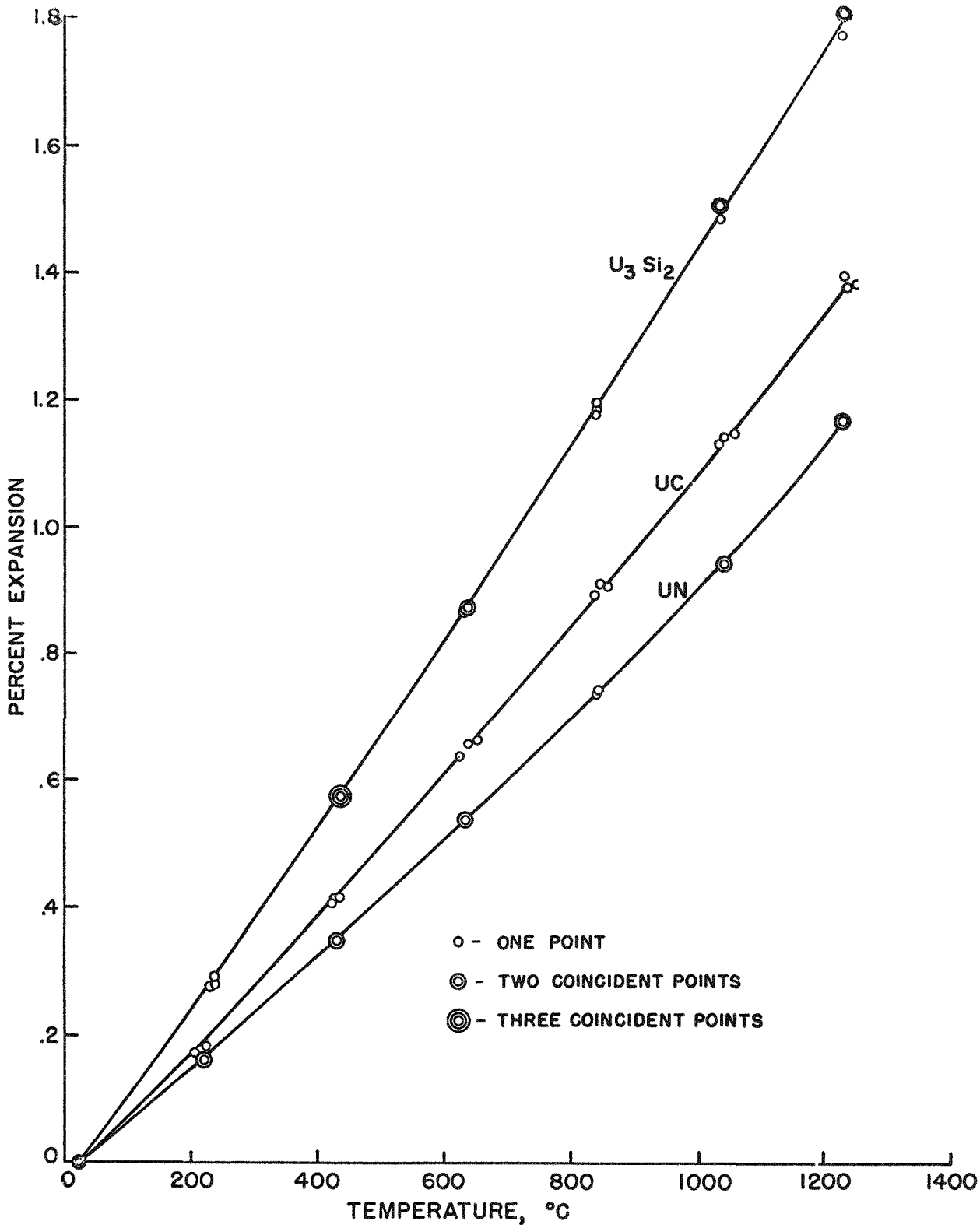
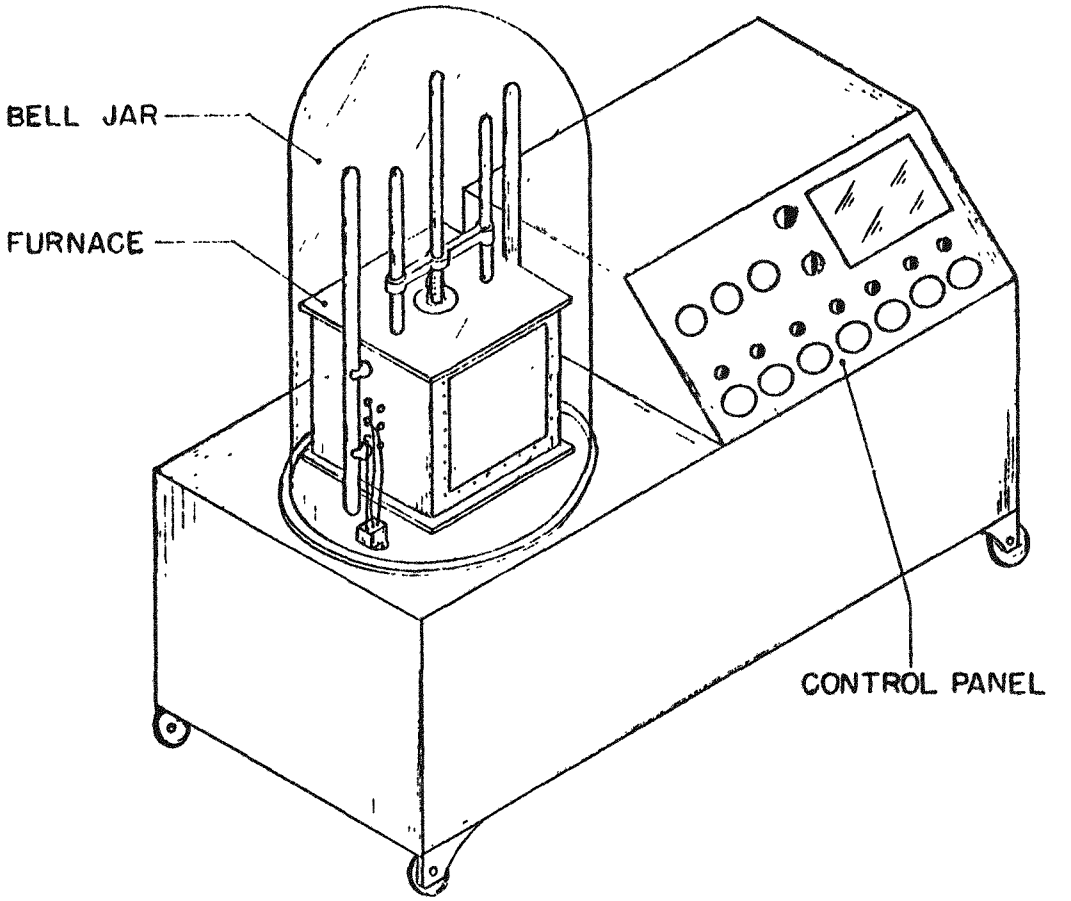


Figure 17 - INERT ATMOSPHERE DILATOMETER

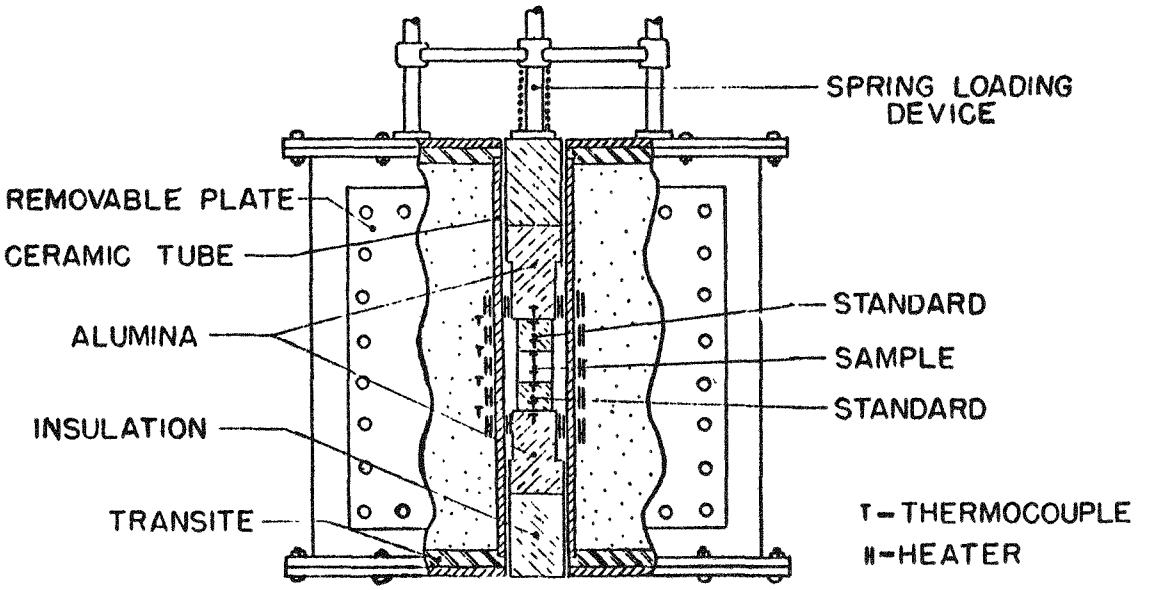


THERMAL EXPANSION OF UC, UN, $U_3 Si_2$

FIGURE 18

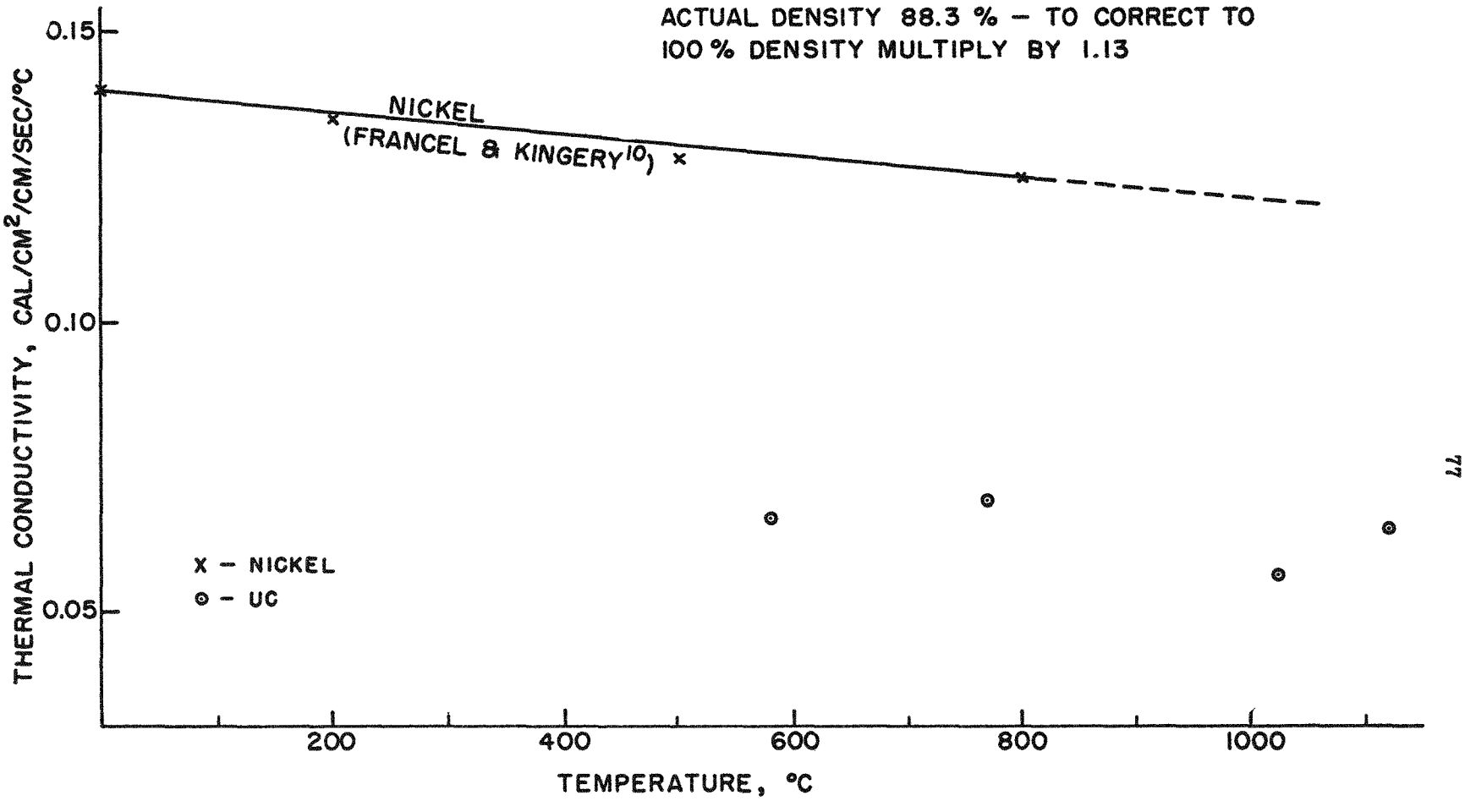


PRECISE THERMAL CONDUCTIVITY APPARATUS (1200°C)



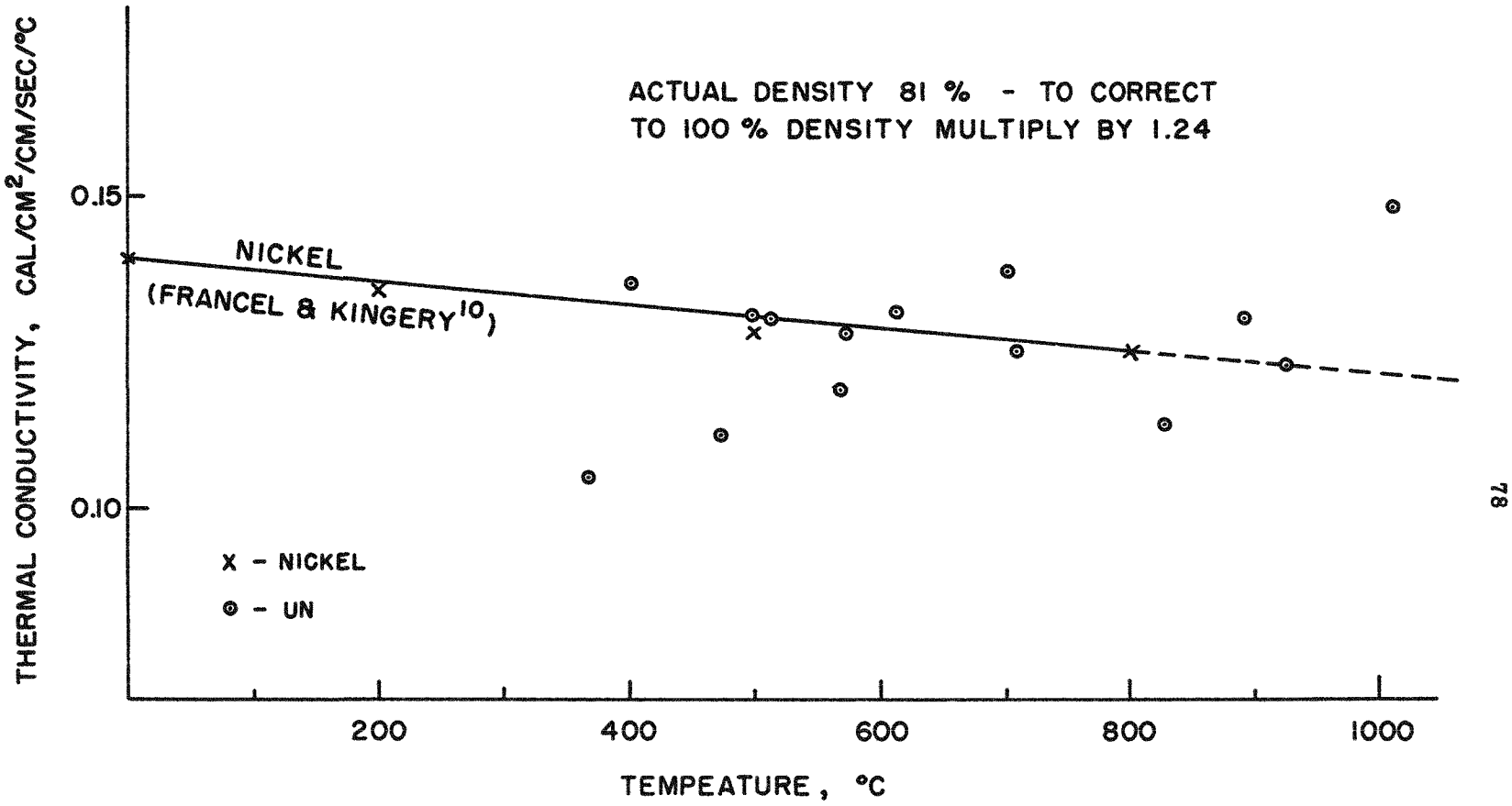
FURNACE DETAIL

Figure 19



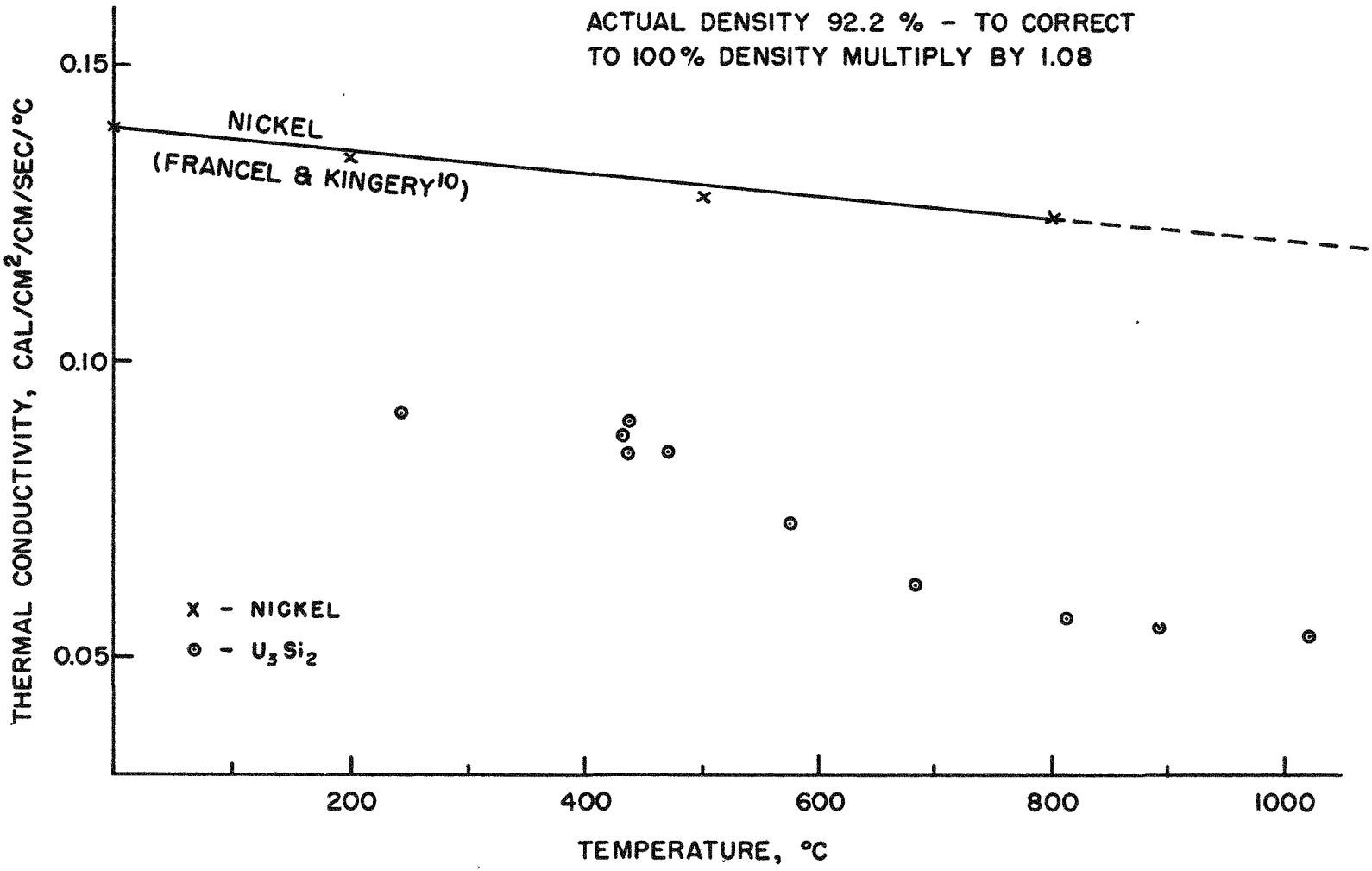
TENTATIVE THERMAL CONDUCTIVITY OF UC AS COMPARED TO NICKEL

FIGURE 20



TENTATIVE THERMAL CONDUCTIVITY OF UN AS COMPARED TO NICKEL

FIGURE 21



TENTATIVE THERMAL CONDUCTIVITY OF U_3Si_2 AS COMPARED TO NICKEL

FIGURE 22

HIGH TEMPERATURE
MODULUS OF RUPTURE
APPARATUS
(CUT AWAY VIEW)

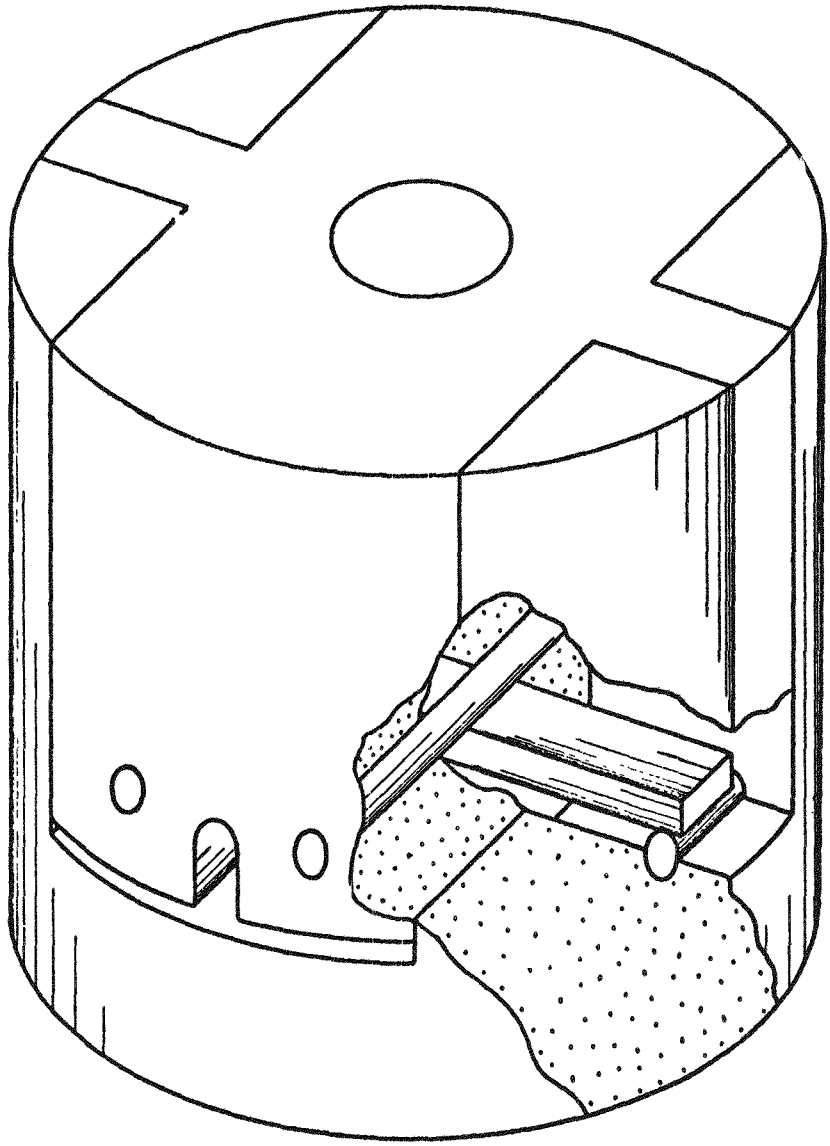


Figure 23

HIGH TEMPERATURE MODULUS OF RUPTURE APPARATUS

(ASSEMBLY DRAWING)

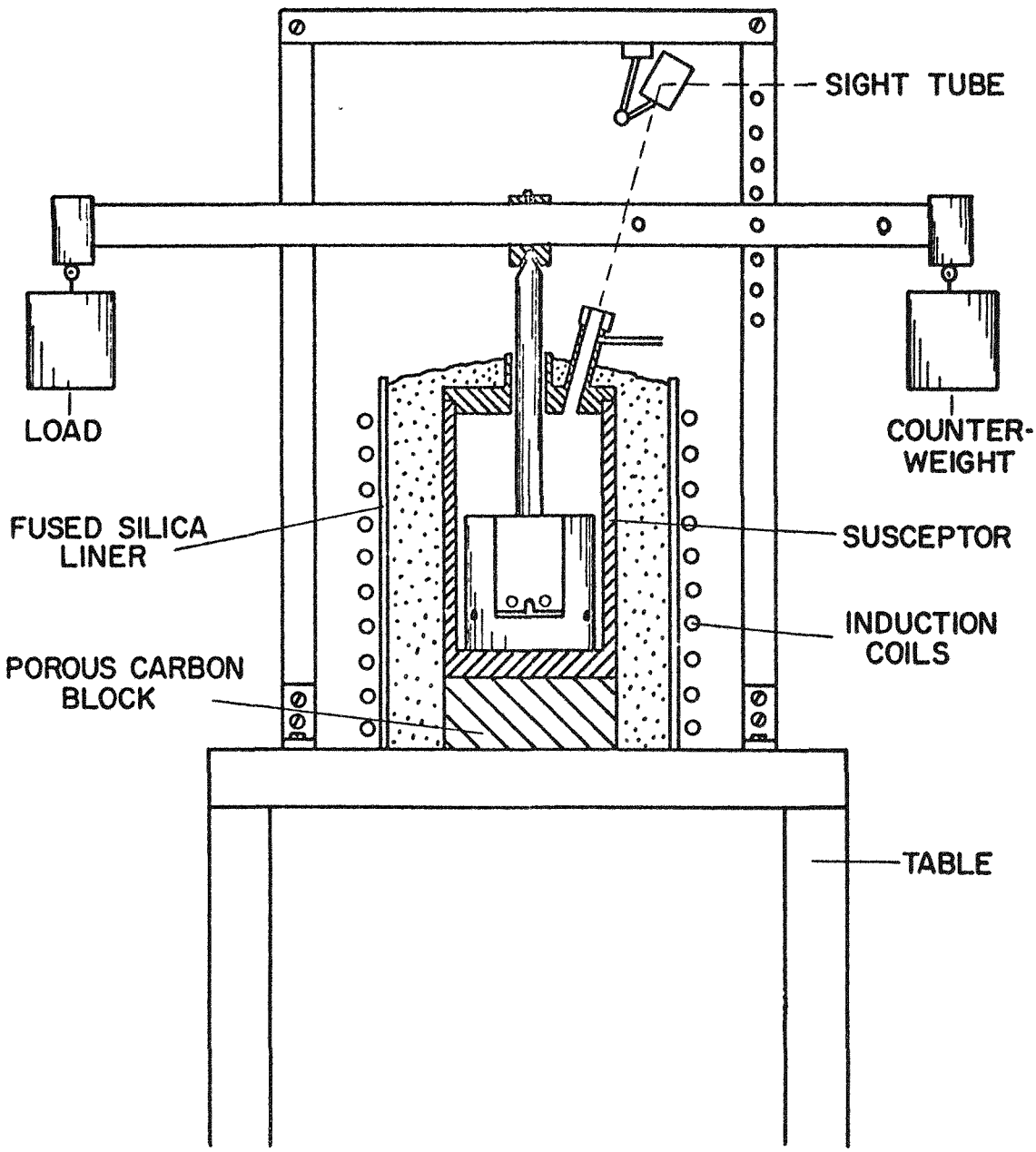


Figure 24

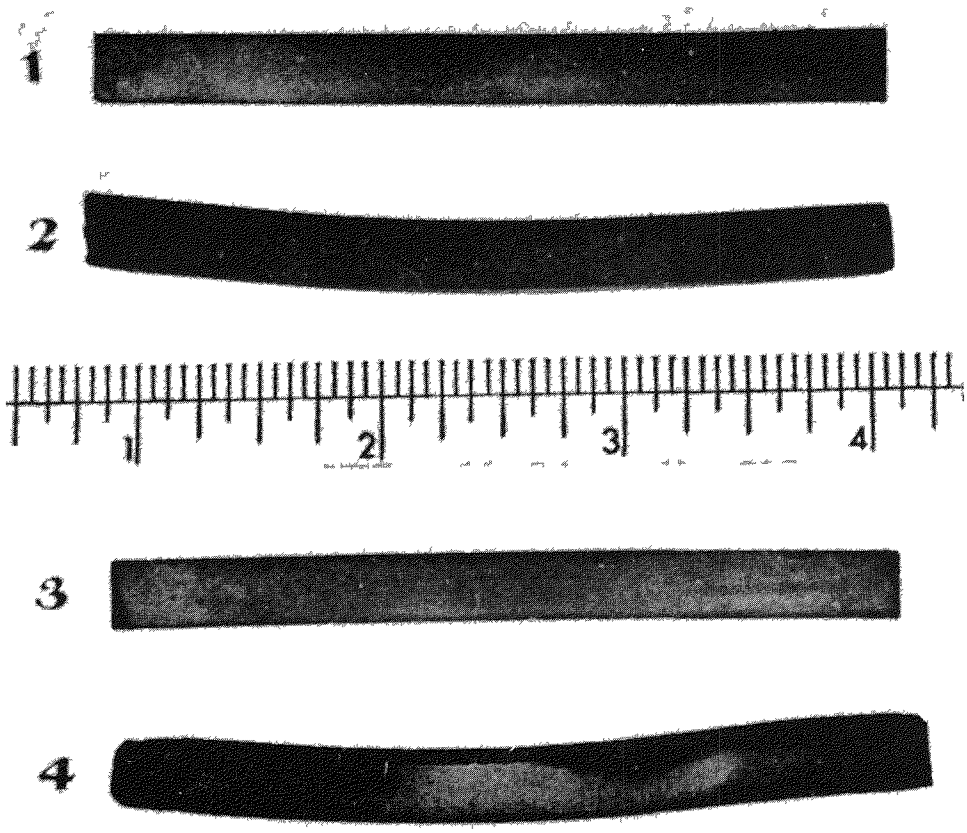


Figure 25 - 1. UC Bar Before Testing.
2. UC Bar After Loading At 1200°C.
3. UN Bar Before Testing.
4. UN Bar After Loading at 1600°C.

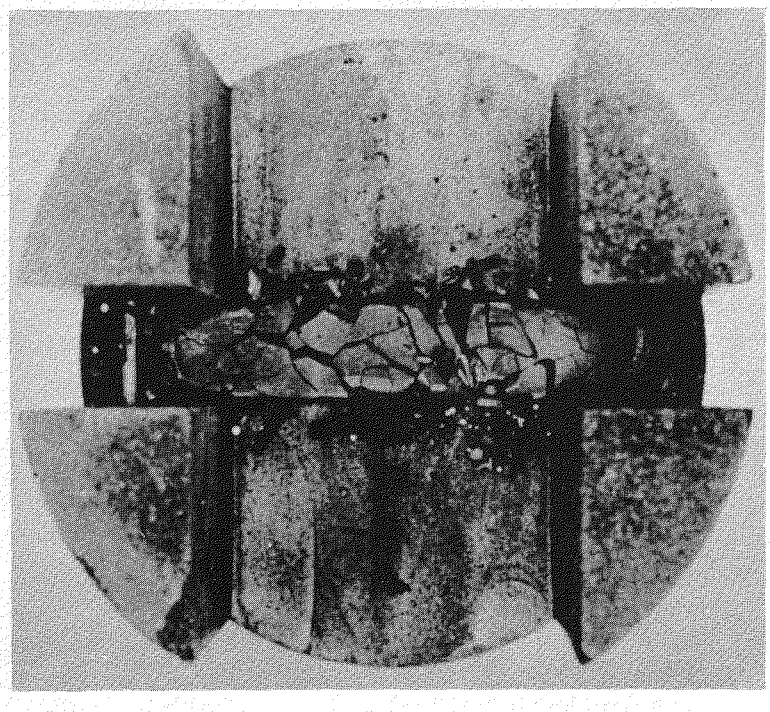
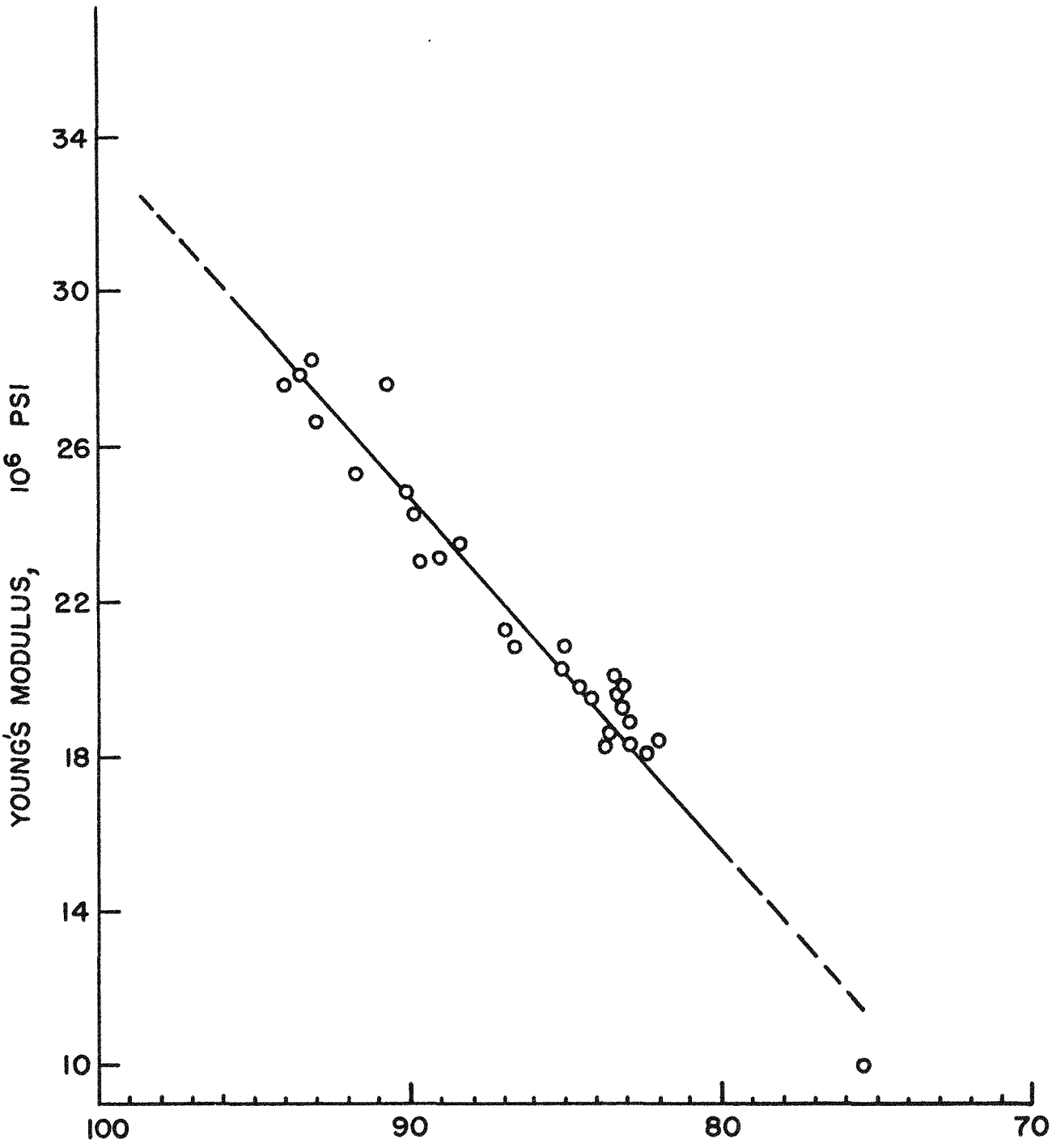
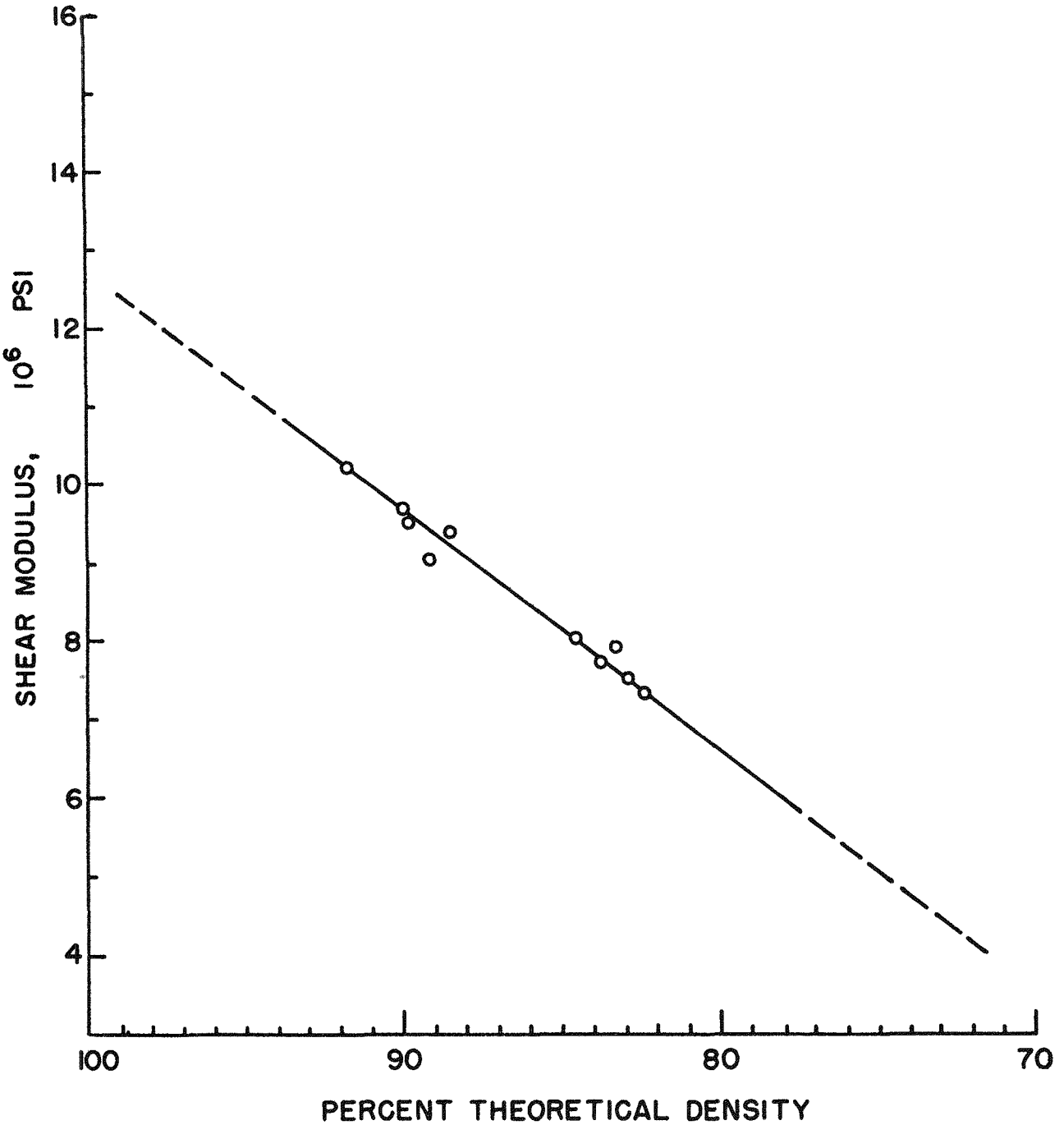


Figure 26 - U_3Si_2 Bar After Modulus of Rupture Test at 800°C. The disintegration was probably caused by oxidation during slow cooling in the furnace after completion of the test.



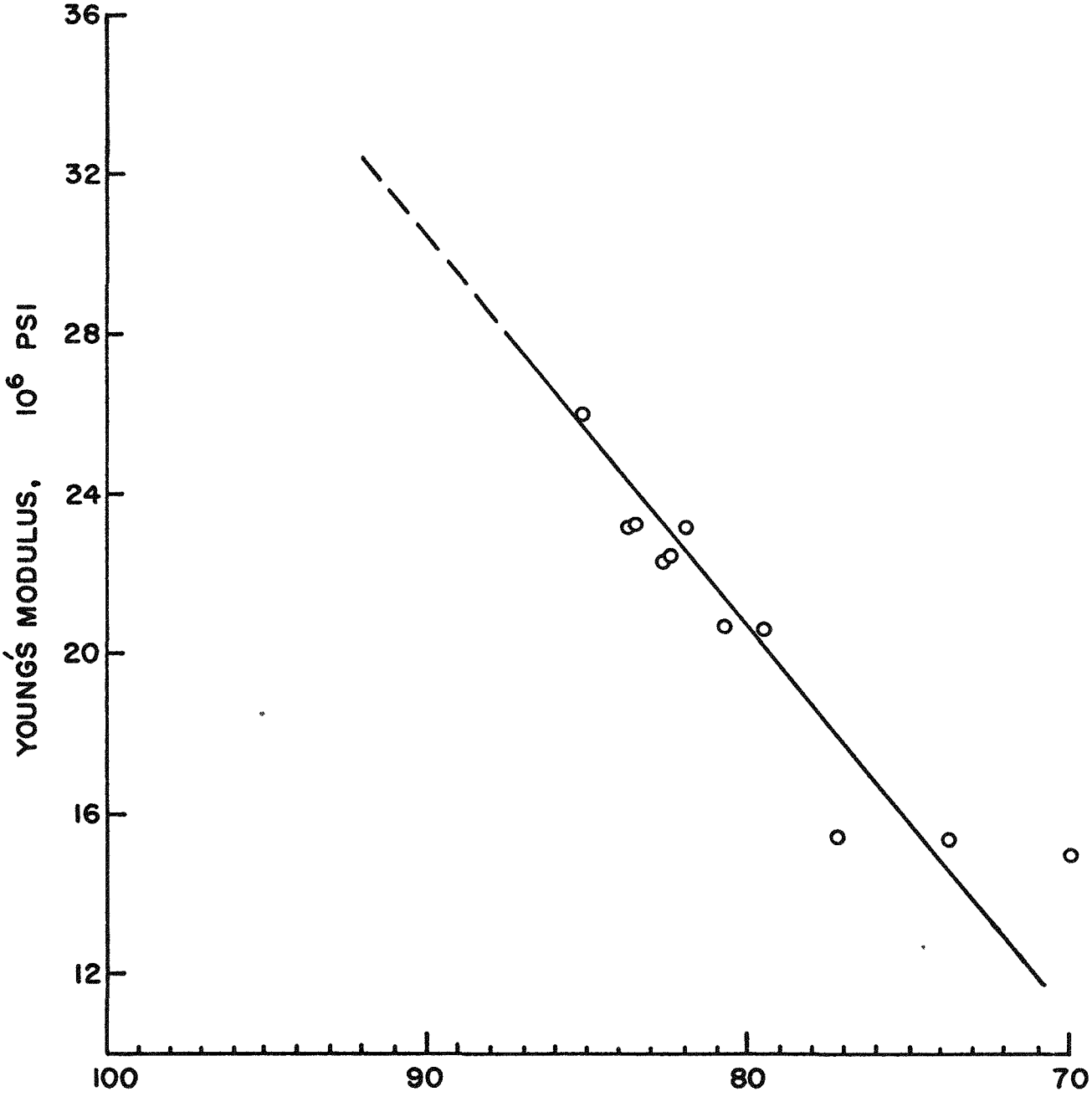
VARIATION OF YOUNG'S MODULUS OF UC WITH DENSITY

FIGURE 27



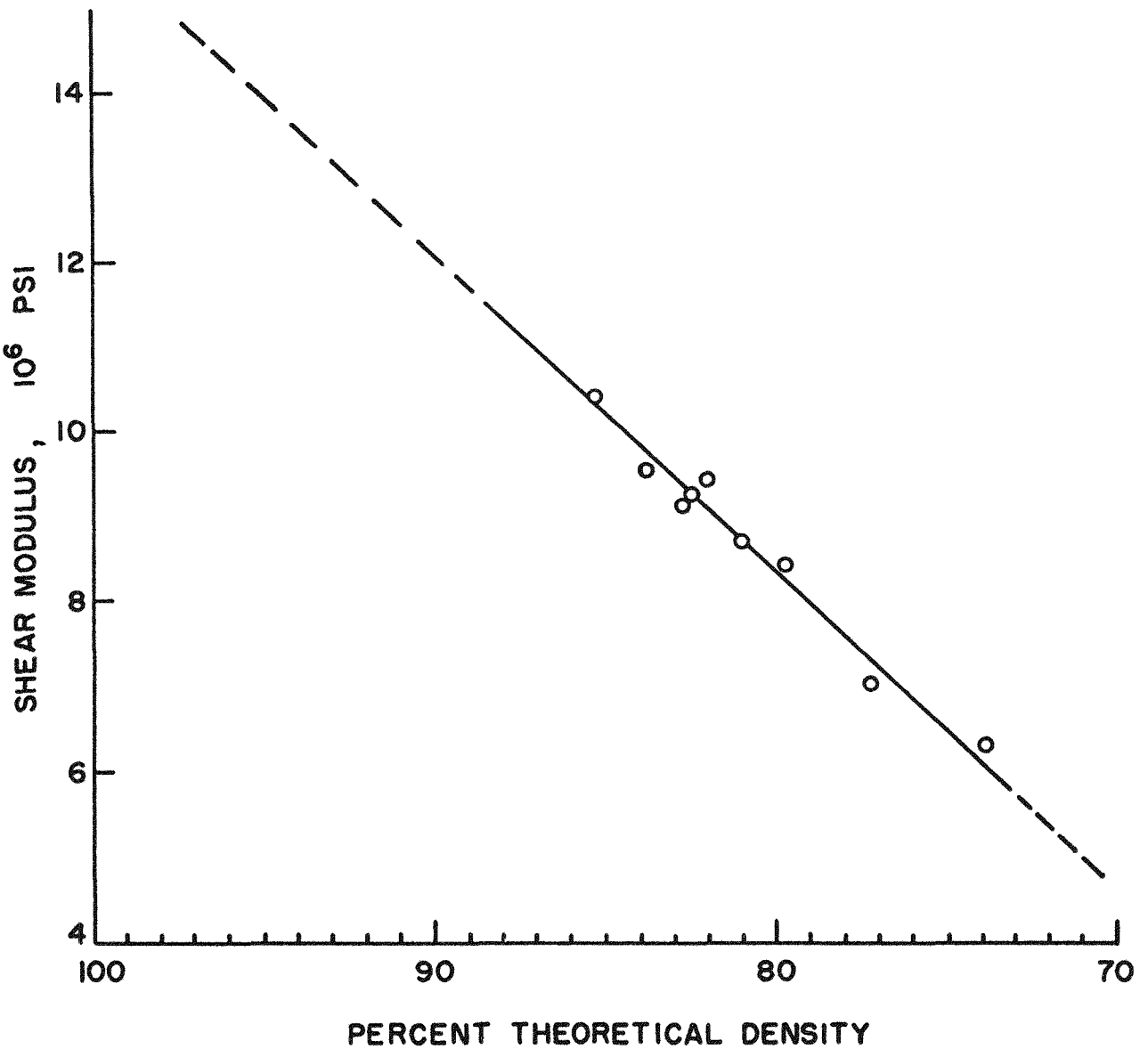
VARIATION OF SHEAR MODULUS OF UC WITH DENSITY

FIGURE 28



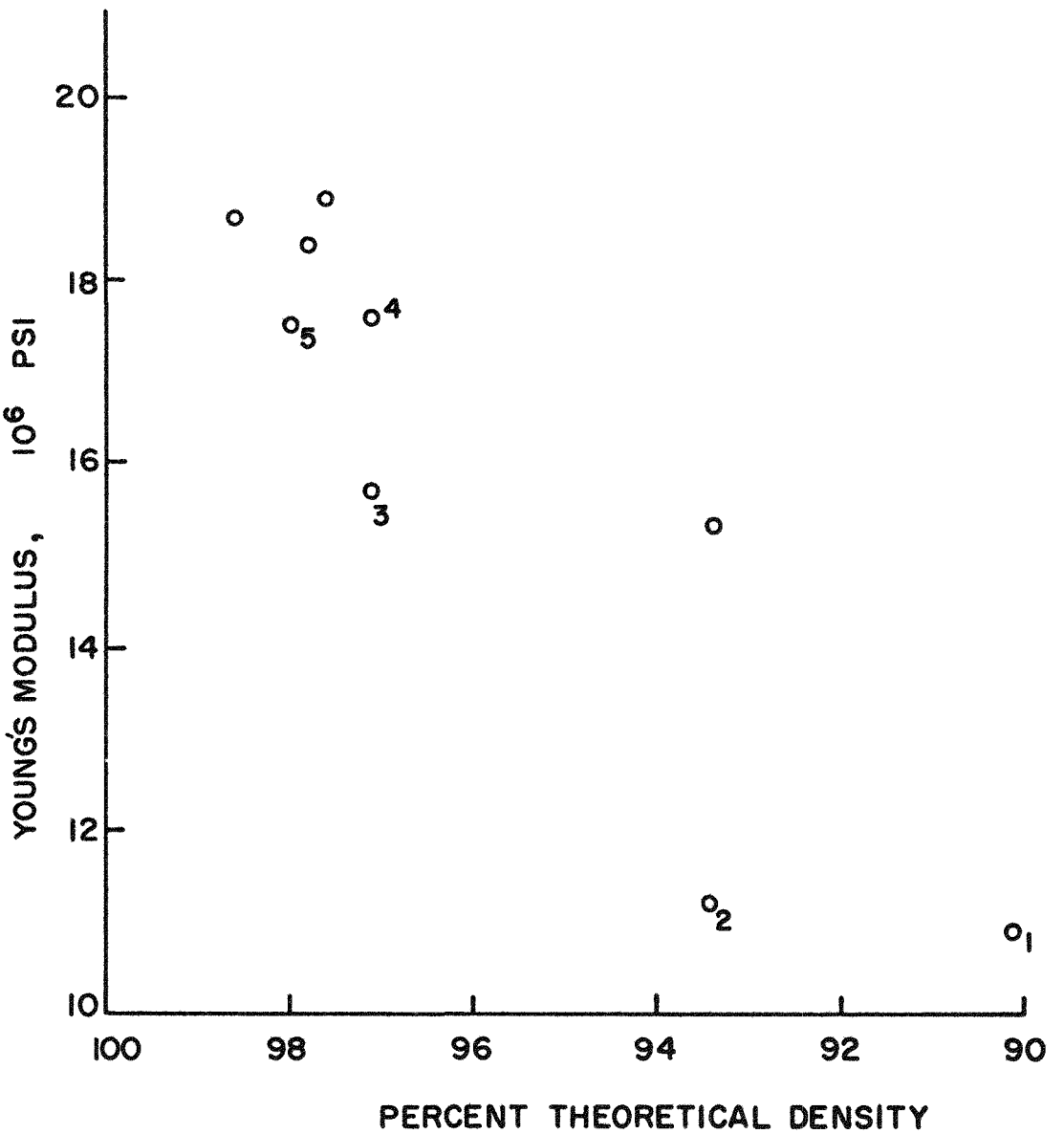
VARIATION OF YOUNG'S MODULUS OF UN WITH DENSITY

FIGURE 29



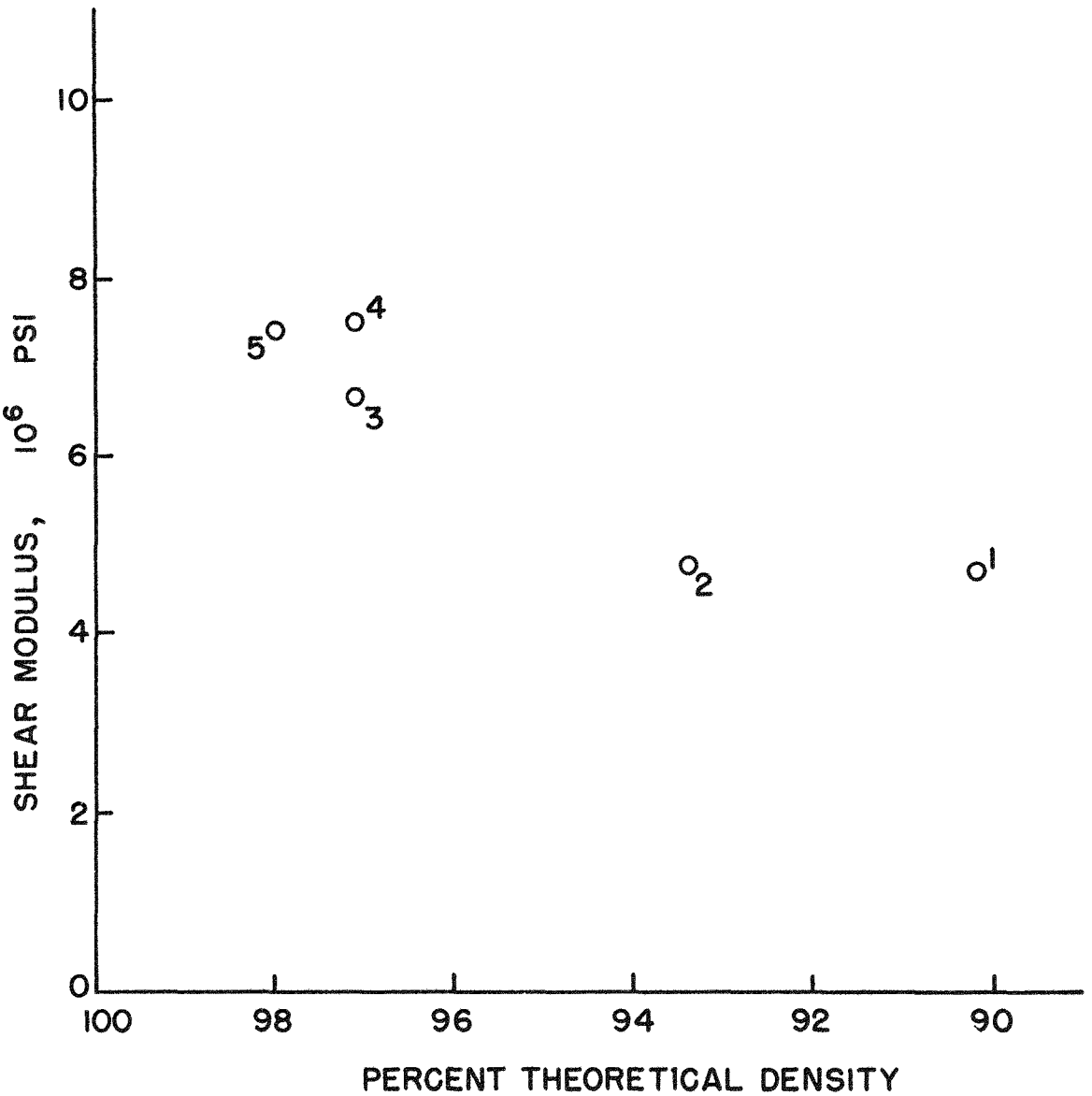
VARIATION OF SHEAR MODULUS OF UN WITH DENSITY

FIGURE 30



VARIATION OF YOUNG'S MODULUS OF U_3Si_2 WITH DENSITY

FIGURE 31



VARIATION OF SHEAR MODULUS OF U_3Si_2 WITH DENSITY

FIGURE 32

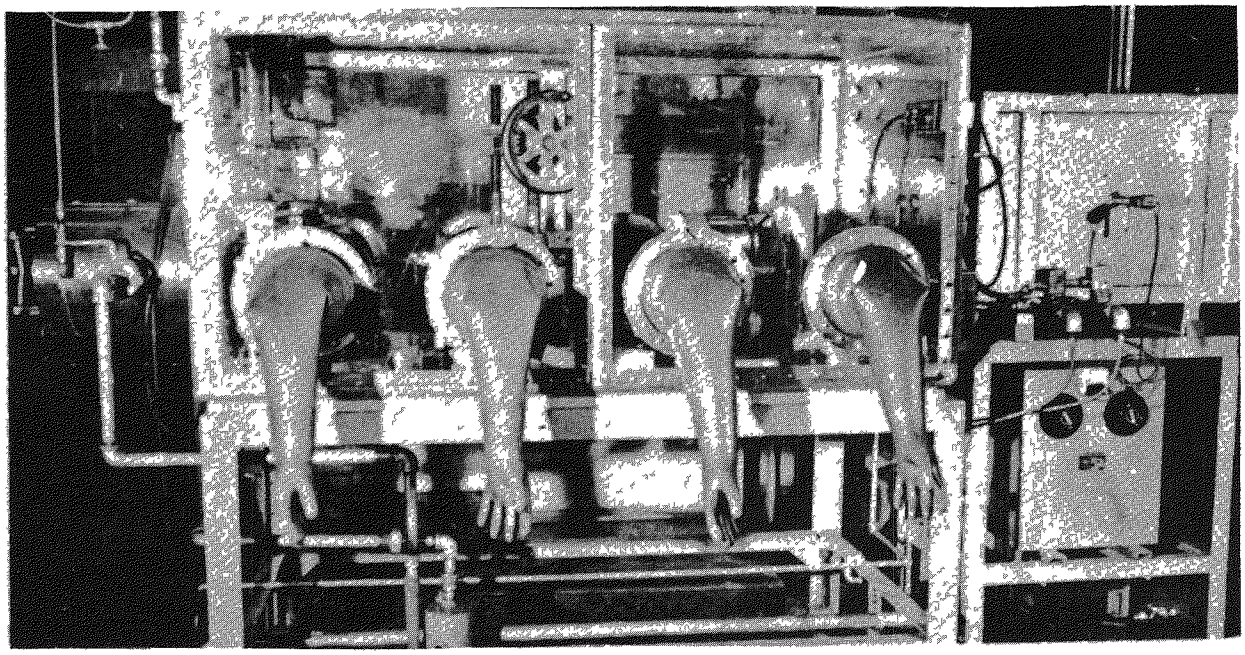


Figure 33a - Glove Box With Attached High Temperature Furnace.

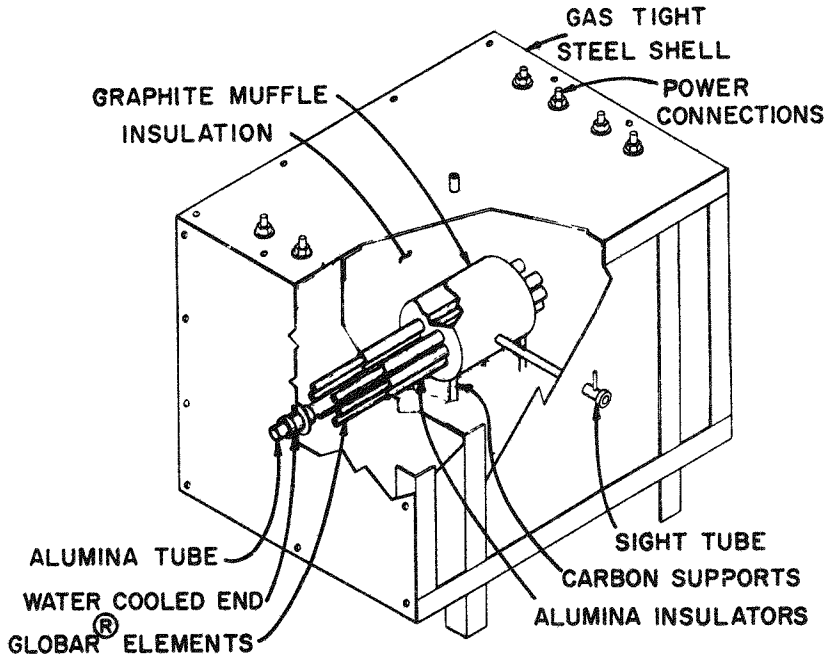


Figure 33b - Details of High Temperature Furnace.