

10-1964

The carbon reduction of uranium oxide

H. A. Wilhelm
Iowa State University

Follow this and additional works at: http://lib.dr.iastate.edu/ameslab_isreports



Part of the [Ceramic Materials Commons](#), and the [Metallurgy Commons](#)

Recommended Citation

Wilhelm, H. A., "The carbon reduction of uranium oxide" (1964). *Ames Laboratory Technical Reports*. 86.
http://lib.dr.iastate.edu/ameslab_isreports/86

This Report is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Technical Reports by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

The carbon reduction of uranium oxide

Abstract

The preparation of uranium metal directly from its oxides has been studied by a number of investigators. Various approaches have been pursued in these studies. Some attempts to produce the metal by electrolysis of the oxide in fused salt have been made; however, the reductions of the oxides by another metal and by carbon have attracted most attention. Although no entirely satisfactory method has yet been developed for preparation of uranium metal directly from oxide, the ready availability of high purity oxides makes such a process of interest. An investigation dealing with an approach to this problem is reported here.

Disciplines

Ceramic Materials | Metallurgy

IS-1023



IOWA STATE UNIVERSITY

**THE CARBON REDUCTION OF
URANIUM OXIDE**

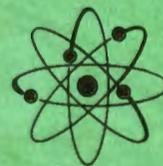
by

H. A. Wilhelm

AMES LABORATORY

**RESEARCH AND
DEVELOPMENT
REPORT**

U.S.A.E.C.



PHYSICAL SCIENCES READING ROOM

IS-1023

Metals, Ceramics, and Materials (UC-25)
TID-4500 October 1, 1964

UNITED STATES ATOMIC ENERGY COMMISSION
Research and Development Report

THE CARBON REDUCTION OF
URANIUM OXIDE

by

H. A. Wilhelm

October, 1964

Ames Laboratory
at
Iowa State University of Science and Technology
F. H. Spedding, Director
Contract W-7405 eng-82

This report is distributed according to the category Metals, Ceramics, and Materials (UC-25), as listed in TID-4500, October 1, 1964.

LEGAL NOTICE

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

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

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

Printed in USA. Price \$ 2.00 Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

CONTENTS

	Page
I. INTRODUCTION	5
II. HISTORICAL REVIEW	7
III. MATERIALS AND CHARGE CONSIDERATION	12
1. Carbon	12
2. Uranium Oxides	13
IV. SOME FUNDAMENTAL CONSIDERATIONS.	14
V. EXPERIMENTAL RESULTS AND DISCUSSION	19
BIBLIOGRAPHY	38

IS-1023

THE CARBON REDUCTION OF URANIUM OXIDE*

H. A. Wilhelm

I. INTRODUCTION

The preparation of uranium metal directly from its oxides has been studied by a number of investigators. Various approaches have been pursued in these studies. Some attempts to produce the metal by electrolysis of the oxide in fused salt have been made; however, the reductions of the oxides by another metal and by carbon have attracted most attention. Although no entirely satisfactory method has yet been developed for preparation of uranium metal directly from oxide, the ready availability of high purity oxides makes such a process of interest. An investigation dealing with an approach to this problem is reported here.

The metals that have received major attention as reductants for uranium oxide include aluminum, magnesium and calcium. The product obtained by the aluminum reduction at elevated temperature is, however, always highly contaminated with aluminum. The magnesium reaction which requires high temperature and high pressure, has not shown sufficient promise to warrant development beyond the experimental stage. Calcium, the most favorable of these three metals as a

* This paper was originally presented at the American Chemical Society's 1960 Midwest Award Symposium held November 12 at Lauderman Hall, Washington University, St. Louis, Missouri.

reductant for uranium oxide, has been employed in a number of laboratories to obtain fair quality uranium metal powder by carrying out the reduction at temperatures around 1000°C. Massive uranium may then be prepared from this product by powder metallurgy techniques. In studies of electrolysis of uranium oxides dissolved in fused-salts, the main deterrent appears to be that of obtaining a suitable fused-salt composition in which a certain oxide of uranium is sufficiently soluble. The carbon reduction of uranium oxides has been studied by many investigators and a survey of some of their work together with discussion of work in progress on this reduction is reported here.

There are advantages and disadvantages in the method of carbon reduction of uranium oxide as compared to some other methods for preparing the metal. A comparison particularly with the magnesium reduction of uranium tetrafluoride is of interest. Some of the advantages of carbon reduction of uranium oxide compared to the UF_4 -Mg method are pointed out here; the disadvantages or limitations of this carbon reduction will become evident in later developments in this report.

In considering the two reactions:



let us assume that uranium oxide with adequate purity is available for direct preparation of satisfactory metal. Two cost factors based on

materials stand out prominently in favor of the carbon reduction. First, the preparation of UF_4 , which is prepared from uranium oxide, is not needed; and second, the amount of carbon required is less than the amount of the more costly magnesium needed for preparing the same amount of uranium product. The impurities introduced by carbon in the charge could be very low. These advantages of the carbon reduction offer inducements to extend the investigation of this reduction in an effort to determine conditions for putting such a method on a practical operating basis.

II. HISTORICAL REVIEW

Historically, carbon reduction of uranium oxides is not, in any sense, a recent approach to the preparation of uranium metal. Klaproth discovered uranium in 1789 when he prepared a yellow oxide of the element from an extract from pitchblend. His attempts to prepare the metal from this oxide were based on carbon reduction. He mixed the oxide with linseed oil and burned the mass gently to a black heavy powder which he then placed in a crucible lined with charcoal dust. The charge was covered with more charcoal powder before placing a lid on the crucible. This assembly was placed in a moderately heated furnace and the resulting product was a heavy mass of loose consistency that could be recovered from the charcoal dust. He continued this work by adding calcined borax to a similar charge which was then heated to the highest temperature obtainable with his furnace. He assumed the dark porous granular product which he obtained to be

the free element and, because of its brittle nature, to be somewhat of a half-metal. Klaproth's work was repeated by a number of workers in his time and it was believed that the new element, uranium, presented not the slightest difficulty of production in the metallic state.

A half century passed before it was demonstrated by Peligot that Klaproth's method did not give metal, but gave a lower oxide. However, Moissan more than a century after Klaproth's experiments demonstrated that uranium metal could be obtained by carbon reduction of oxide. Moissan at that time had available an electric-carbon-arc furnace that was capable of heating the charge of oxide and sugar charcoal to the high temperature required for the reduction. However, Moissan's carbon reduced metal always contained sufficient carbon to cause it to be brittle. Aloy in the early part of this century repeated Moissan's work and also came up with poor quality metal.

Early in 1942 when uranium metal became important to the atomic energy program in America, a group in the Chemistry Department at Iowa State briefly explored a number of reported methods for the preparation of the metal as a part of a uranium metal development program. Included was the carbon reduction of uranium oxide which, according to some review reports of Moissan's work, was possibly capable of giving good metal. Vacuum induction heating equipment was employed in this study, and repeatedly the metal contained carbon in excessive quantities. Study of this process was discontinued then in this exploratory work since it appeared that some problems not immediately solvable stood in the way and there were other avenues for

possible metal preparation still open for investigation. Return to the carbon reduction for that immediate emergency would be done only in case nothing appearing better at the time was derived.

Other readily expandable methods were found for metal preparation; these were developed into pilot-plant and then large-scale production to meet the demands of the wartime project. Casual interest in exploring further the potentiality of the carbon reduction remained, however.

Because of a number of other somewhat pressing problems in the area of metallurgical research, after the establishment of the atomic program under the U. S. Atomic Energy Commission, in 1946, little effort was again directed in this country toward the carbon reduction of uranium oxide until about 1953. In that year workers at Sylvania did some exploratory work that led to an expanded effort on this reduction. Pilot plant operations were set up on a 100 pound batch basis at Sylvania-Corning, and by 1957 the process developed there had been tested and evaluated. It has been stated that the Sylvania process is close economically to the present large scale UF_4 -magnesium process for uranium metal.

The process derived at Sylvania-Corning was based essentially on the product of the reaction as obtained by Moissan three score years earlier. The metal obtained by Moissan, and also that prepared by carbon reduction at Ames in 1942, contained sufficient carbide to embrittle the metal. The Sylvania-Corning approach was to prepare this brittle metal in massive (or biscuit) form, break up the biscuits,

hydrolyze the carbide, physically separate most of the resulting oxide, acid leach the residual oxide and recover the uranium metal in the form of a loose spongy mass that could be further processed to give compact metal.

Figure 1 is a diagram representing the major operations in the Sylvania process. A number of conditions of operation connected with this process bear on the quality and yield of the final product.

Some of the more important conditions include: (1) The charge has to be heated to well above 2000°C in a vacuum to obtain adequate reaction. (2) The brittle product is pyrophoric when hammered, so must be forged or deformed in an inert atmosphere. (3) The hydrolyzing temperature must be so controlled that the hydrolysis of the carbide takes place at a practical rate while the metal-water reaction is not appreciable. (4) The nitric acid pickle has to be well controlled also to give solution of the residual oxide without forming an appreciable oxide coat on the metal. (5) Since the sponge metal product has a high surface to volume ratio it must be handled and stored with care to prevent loss of metal by fire or conversion back to oxide. (6) Although the quality of the metal appears to be satisfactory, the yield of metal per charge is low. In each cycle only about one third of the starting uranium, in the form of UO_2 , is obtained as metal.

Although an evaluation of the Sylvania process employing the carbon- UO_2 reaction appears to place this process close economically to the present UF_4 -Mg process, if any net advantage does exist it is not of sufficient concern to warrant an effort to replace the present

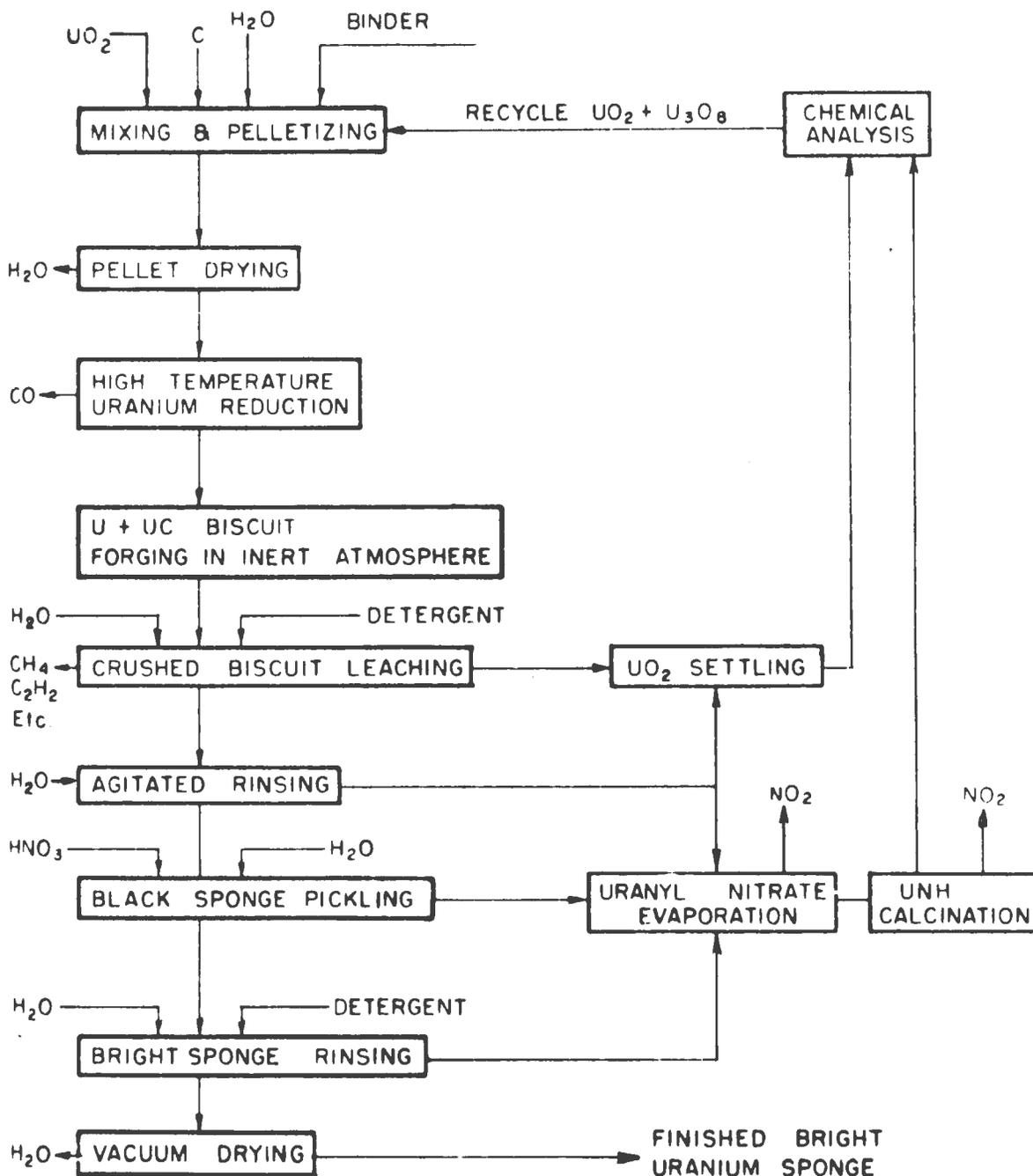


Fig. 1. Diagram representing the Sylvania process for uranium.

operations. Had the Sylvania process been developed first and large scale production plants established and further refinements and developments made through experience with the process, the reverse situation might then have existed.

III. MATERIALS AND CHARGE CONSIDERATION

1. Carbon

Carbon for the reduction of oxides is available in various forms, purities, particle sizes and packing densities. Low ash content carbon is desired and for purity of final metal the composition of the ash must also be considered. Many grades of carbon having less than 0.2 % ash are available commercially. The components of the ash are generally expressed as FeO, CaO, MgO, SiO₂, Al₂O₃ and very minor amounts of a few other oxides. In the high temperature processing some of these elements are eliminated. If the charge is to be made up to a closely controlled composition then the volatile matter content in the carbon should be low or quite well known. Some carbons have as much as 3 % volatile matter while other carbons have practically no volatile matter.

Solid-solid reactions, solution and diffusion all quite likely have important roles in the over-all process and these should be favored by preparing the charge with thoroughly mixed finely divided materials. The carbons available vary in particle size from a few microns in carbon blacks to fairly coarse granules in some graphites.

Another consideration is the packing density of the carbon used in

making up the charge. If more uranium can be contained in the charge packed into a certain volume crucible, then more product metal per charge should result. The packing densities of some carbons of the acetylene-black type are so low that the packed volumes of charges prepared with them are about double those of charges containing equal uranium but made with some of the more dense carbons.

2. Uranium Oxides

A number of anhydrous oxides of uranium are known to exist. The yellow oxide (UO_3) was possibly the oxide which Klaproth employed in his efforts to prepare elemental uranium. The green-black oxide (U_3O_8) was mixed with sugar charcoal in the charges employed by Moissan in his studies of the preparation of metallic uranium by carbon reduction of oxide. The brown oxide (UO_2) received most attention by workers at Sylvania-Corning in the development of their process.

The composition of the brown oxide, however, is not always exactly UO_2 . Quite often the composition will be higher in oxygen content. Compositions of about $\text{UO}_{2.14}$ are common and even a composition of $\text{UO}_{2.25}$ (U_4O_9) is known to exist as possibly a solid solution extending from UO_2 .

The trioxide can be prepared by thermally decomposing either uranyl nitrate, ammonium diuranate or the peroxide $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. The dioxide, which has the highest uranium density of any of the common oxides can be prepared by heating the trioxide in hydrogen at 600 to 700°C. However, if UO_2 stands exposed to air at room temperature it slowly

picks up oxygen. When it is heated in air at about 800°C, it readily converts to U_3O_8 .

If a charge of oxide plus carbon is made up with any of the oxides having an oxygen content greater than that of UO_2 , the excess oxygen appears to react more readily and the dioxide will become essentially the only oxide composition at some stage in the reduction. A charge consisting of UO_2 and carbon heated in a vacuum to essentially complete reaction at progressively higher temperatures evolves very little gas at temperatures below 1300°C but evolves large quantities of gas around 1500°C. A charge containing UO_3 when heated in a similar manner evolves considerable gas beginning at temperatures as low as 600°C. Most of this low-temperature gas evolution is completed as temperature is increased to 900°C, and above 1000°C the reaction behaves as a charge containing UO_2 . The low temperature reaction, it is assumed, converts the UO_3 to U_3O_8 and in turn to UO_2 .

IV. SOME FUNDAMENTAL CONSIDERATIONS

Since oxygen can combine with carbon to give both CO and CO_2 , the equilibrium conditions for the reaction:



should be given some consideration if a charge of known composition with respect to stoichiometry is to be prepared for carbon reduction of oxides.

Values represented by the curves in Fig. 2 were calculated from

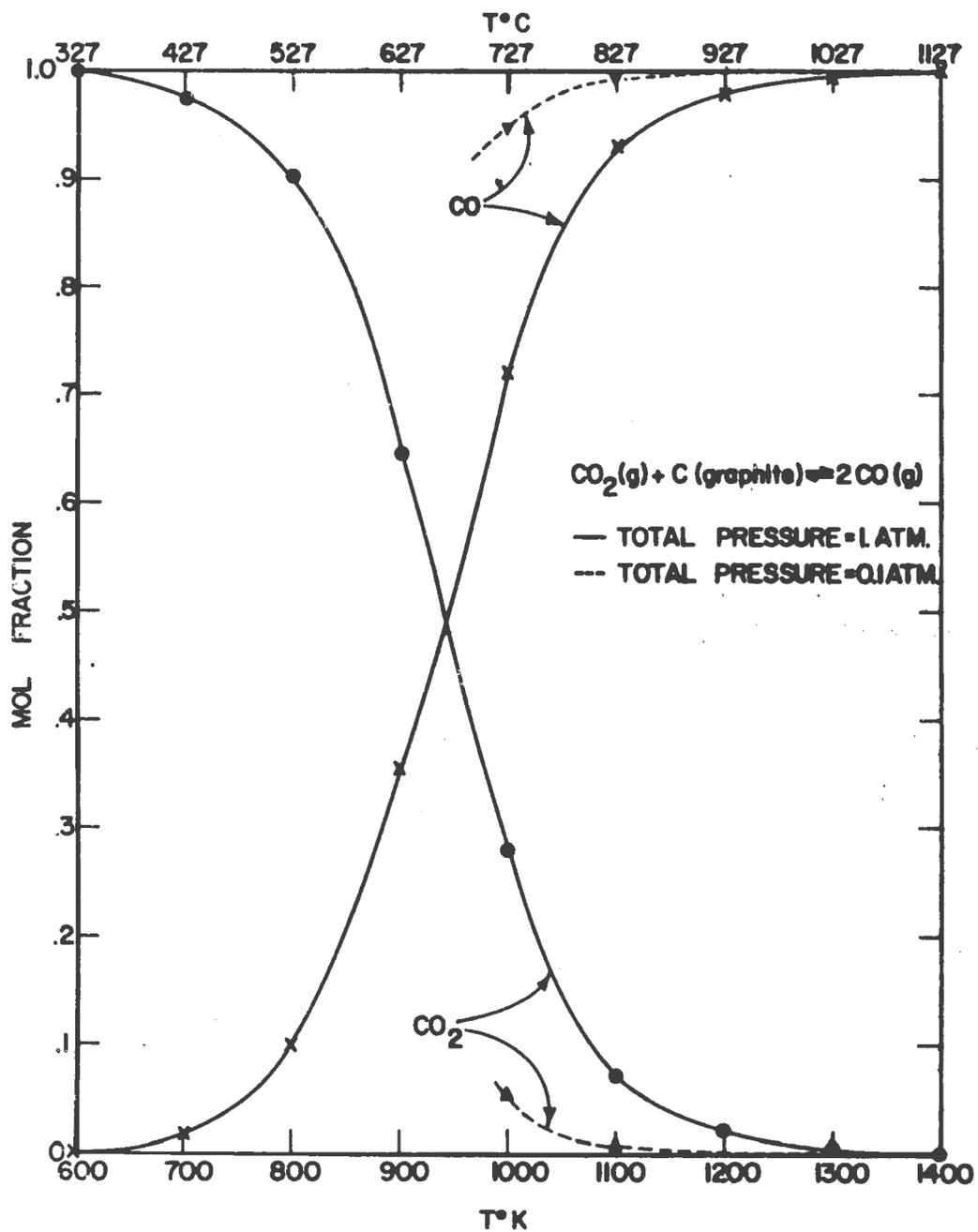


Fig. 2. Calculated temperature - pressure relationships between CO and CO₂ in equilibrium with graphite.

free-energy data for the system containing free carbon (as graphite) and a CO-CO₂ gas phase at equilibrium. It is to be noted that at one atmosphere total pressure the percent of CO in the gas phase increases with temperature to essentially 100 % CO at about 1100°C. If the reaction is carried out at this pressure and over a range of temperatures much below 1000°C, the ratio of CO to CO₂ would be difficult to control or reproduce. If the total pressure on the system is 0.1 atmosphere, the percentage CO in the gas is markedly increased at the lower temperatures. To better control the composition of an oxide-carbon charge with respect to stoichiometry, means for carrying out the reaction at low pressure and high temperature are then desired. It is considered that UO₃ and U₃O₈ and oxides higher in oxygen than UO₂ react in that temperature range where appreciable but unknown or difficultly reproducible amounts of CO₂ could be generated.

In order then to reduce the tendency for possible variation in the gas composition and to have maximum uranium concentration in the charge, uranium dioxide should be used as the source of uranium. The assumed reaction then may be expressed as:



Free energy data are available on the compounds in this expression over a wide range of temperatures. In Fig. 3, the calculated free-energy changes, ΔF° values, for the reaction are almost linear with temperature over the temperature range of interest for reduction. From these free-energy changes, calculated partial pressures of CO

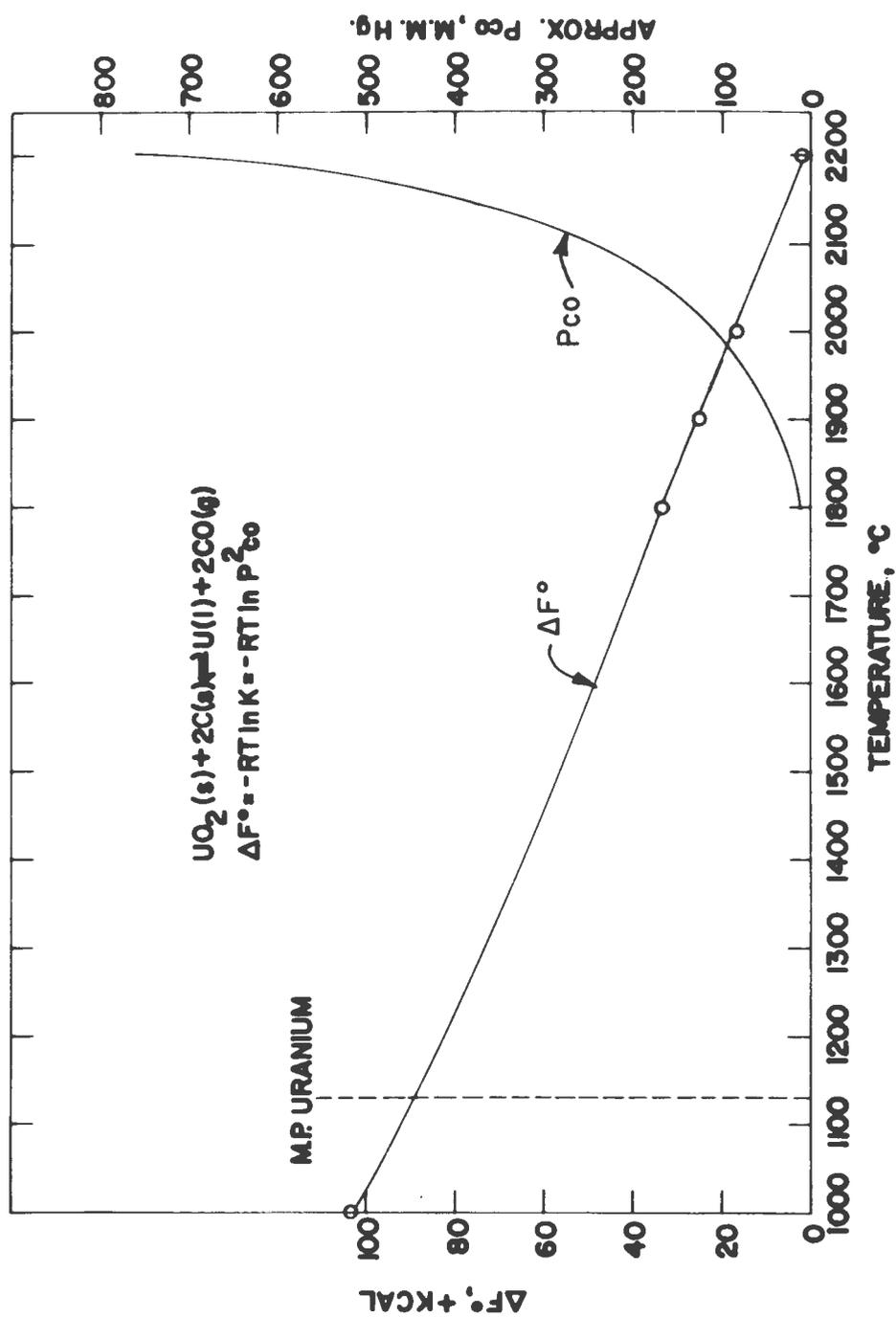


Fig. 3. Calculated free-energy changes and equilibrium pressures of CO for the reaction at various temperatures.

gas in equilibrium with the other components of the reaction at the temperatures of concern are plotted to give the ascending curve to the right. According to the calculations the equilibrium CO pressure should be about 15 mm at 1800°C. If the reaction were as simple as expressed by Eq. (4), above, it appears that the reaction could be driven to completion at 1800°C under rather poor vacuum conditions.

Unfortunately for metal preparation the mechanism of the reaction is not as simple and direct as indicated by Eq. (4). It appears that the reaction takes place in at least two steps that might be represented as follows:



Equation (7) is a sum of Eqs. (5) and (6) and is three times Eq. (4). Insufficient data are available on the components of Eqs. (5) and (6) to make quantitative thermodynamic calculations on conditions for these reactions. However, a rough comparison of Eqs. (4) and (5) would indicate algebraically lower values for the free-energy changes per mol of UO_2 for Eq. (5) at corresponding temperatures if a sizeable negative free energy of formation can be assumed for UC. Therefore, the equilibrium pressures of CO for Eq. (5) would be much greater than for Eq. (4) at all corresponding temperatures. Equation (5) should then proceed readily to the right for charges of UO_2 and carbon heated in vacuum at temperatures that are considerably lower than 1800°C.

A similar rough comparison of Eqs. (4) and (6) would indicate algebraically higher values for the free-energy changes for Eq. (6) at corresponding temperatures. The equilibrium pressures of CO for Eq. (6) would then be much less than for Eq. (4) at all corresponding temperatures. Equation (6) then would require much higher temperatures to generate an equivalent gas pressure or to proceed to completion under equivalent vacuum conditions.

The possibility that UC_2 might also be present over some intermediate range does not change this rough quantitative analysis markedly. If UC_2 does form, the activity of the second carbon is quite likely greater than that of the first carbon (forming UC) but less than that of pure carbon. The tendency of UC_2 to react with UO_2 would then be less than for pure carbon but on reaction would give UC. The effects on the reaction ascribed to the formation of UC would, then, only be extended by the formation of any UC_2 .

V. EXPERIMENTAL RESULTS AND DISCUSSION

Experimental tests on the reaction between UO_2 and carbon are being carried out with vacuum induction heating equipment as shown sketched in Fig. 4. Temperature measurements are made with an optical pyrometer. Pressures are measured by a thermocouple gage. Gas evolution is measured by a wet test meter connected to the exhaust of the mechanical vacuum pump. The charge, packed in graphite or other crucible material, is placed inside a graphite heater that is thermally insulated from the walls of a silica retainer jar. This

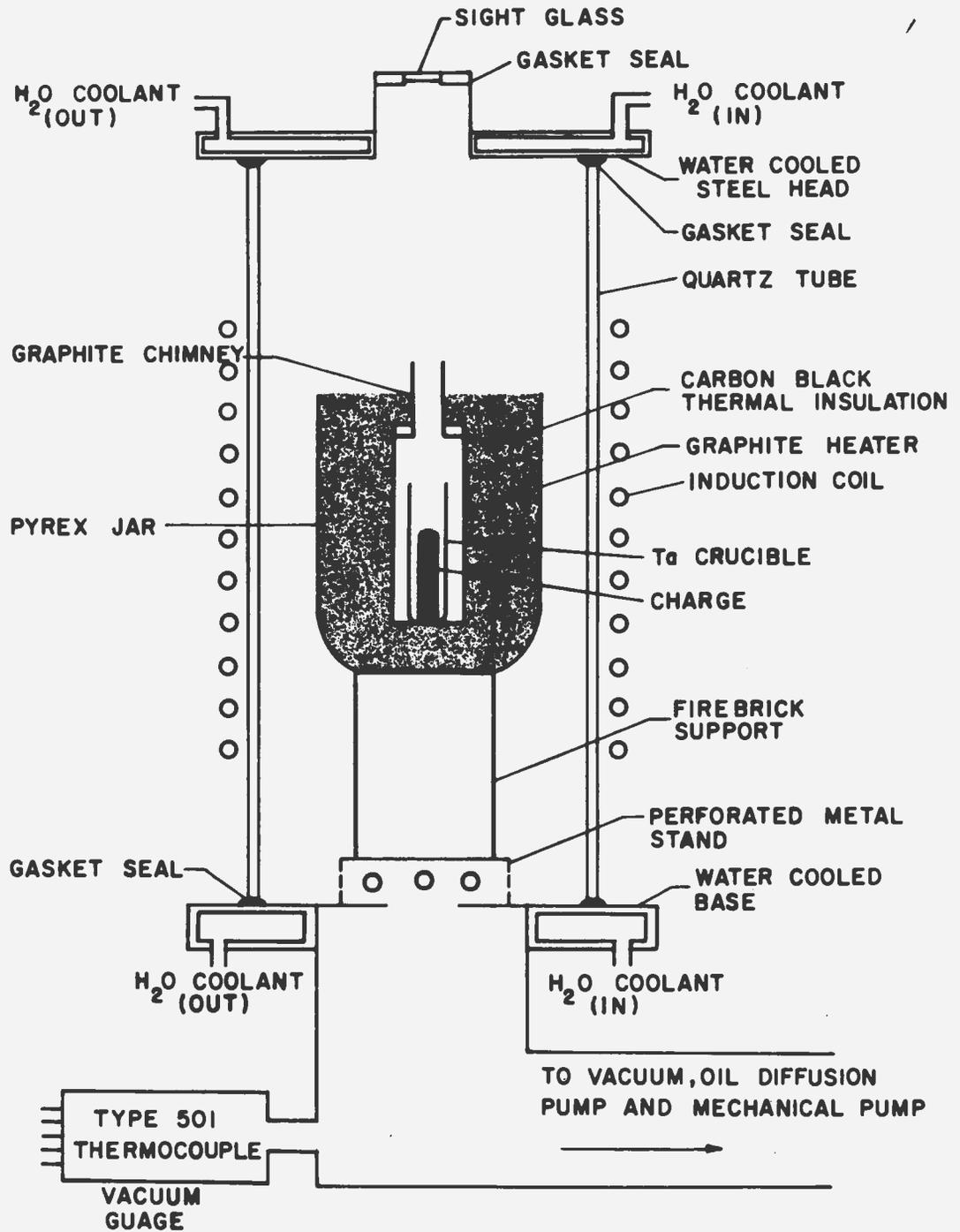


Fig. 4. Cross-section sketch of vacuum-induction furnace.

assembly rests on an insulating base and in a silica tube that is evacuated. The upper end of the silica tube is closed with a water-cooled head having a window for observing the charge and its temperature.

On heating a charge of UO_2 and carbon, essentially no gas is evolved by the charge at temperatures below 1300°C . As the charge is heated to higher temperatures the vacuum gage shows pressure developing in the system and the wet-test meter begins to register volume of evolved gas. An experiment was performed in which the heating of a charge, made up according to Eq. (4), was controlled in stepwise fashion at progressively higher temperatures. Data on the cumulative gas evolution as recorded at the end of each of the temperature intervals are represented by Fig. 5. The pressure at each temperature first rose but the pumping was usually continued until the pressure fell below 10μ before moving to the next higher temperature.

It is to be noted in this figure that a large fraction of the gas is evolved below 1600°C . X-ray and other examinations of an equivalent charge heated similarly but only to this temperature and then removed from the furnace showed essentially UO_2 and UC structures in a spongy product. This would tend to substantiate Eq. (5) or the formation of UC, productwise as an intermediate step in the over-all reaction. Gas evolution from 1600 to almost 2000°C is relatively minor. In the range 2000 to 2050°C the charge again becomes quite active and the reaction is here carried to about 97% completion. It is assumed that a reaction between UC and oxide is the source of the gas evolution over this short temperature range. In order to complete the

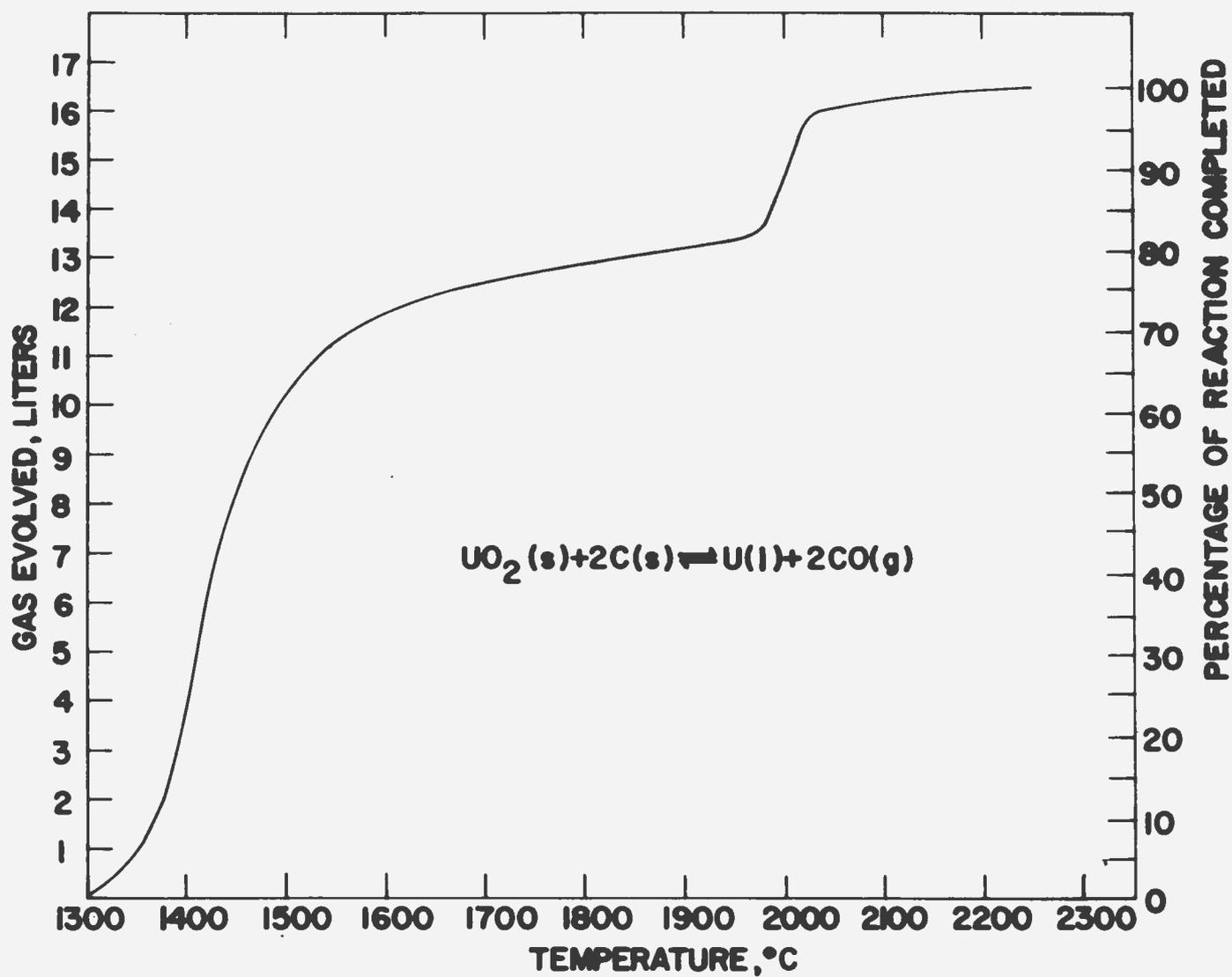


Fig. 5. Cumulative volume of gas evolved as temperature of charge is increased stepwise.

reaction it appears to be necessary, however, to continue heating the product in a vacuum to about 2200°C.

A number of factors bearing on the reaction at these higher temperatures decidedly complicate the picture. In the 2000 to 2050°C range, a liquid phase is observed. This is very likely a uranium metal phase which should be saturated with UC in accordance with the uranium-carbon equilibrium diagram shown in Fig. 6. This solubility effect should, in the early stages of reaction, tend to promote the reaction but at a later stage when the concentration of UC is small the reaction would tend to be retarded. The oxide solubility in uranium metal appears to be very low (see Fig. 7). This degree of solubility should have little deterrent effect on the reaction except at the very final stage.

Before the liquid phase appeared the major means for bringing reactants together was through solid state and gaseous diffusions. Since the liquid-free solid is a somewhat spongy mass, solid-state diffusion is hampered. The vapor pressures of some of the components are relatively high at these temperatures and much of the contact between reactants possibly depends on this phenomenon. Figure 8 shows vapor pressure data for uranium and uranium dioxide, and values of greater than 300 μ are shown for both in the temperature range for the final reaction.

The source of the small amount of gas developed as the charge temperature approaches 2200°C (see Fig. 5) could be the final cleanup of uranium oxide in liquid uranium. Another possible source might be

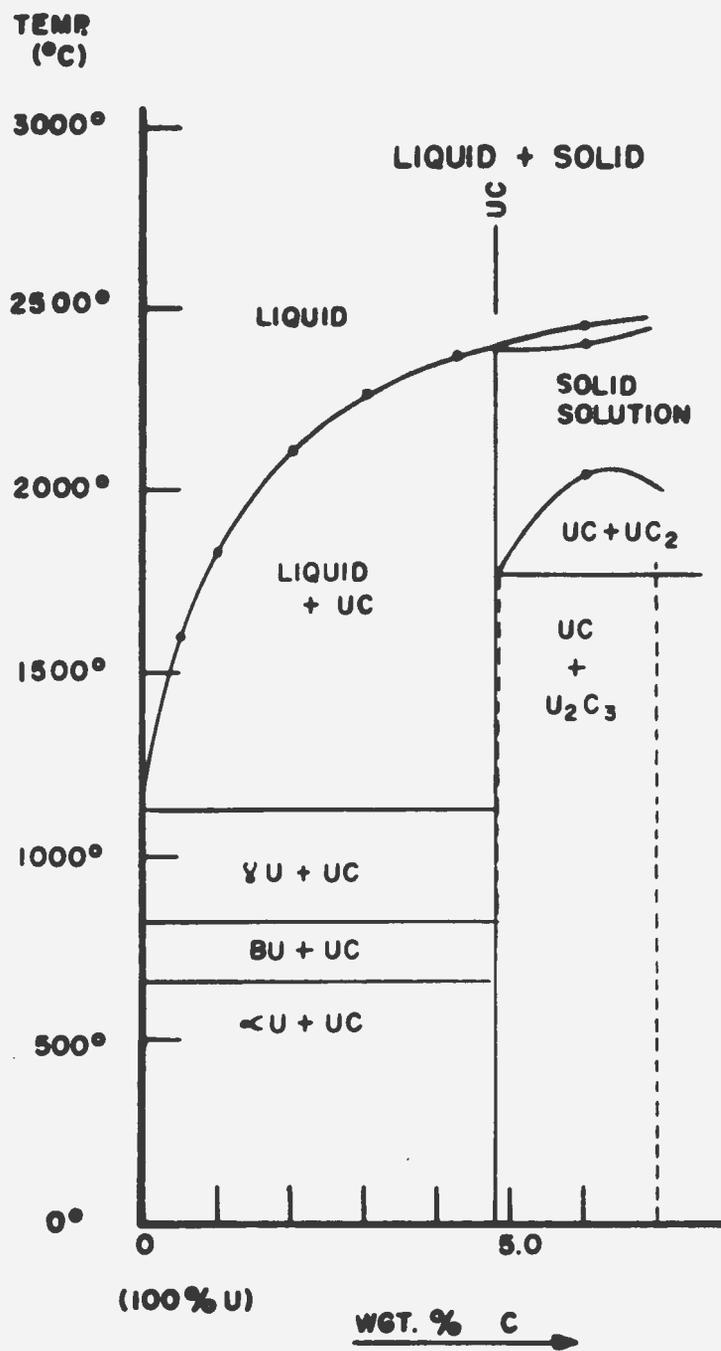


Fig. 6. The uranium-carbon system.

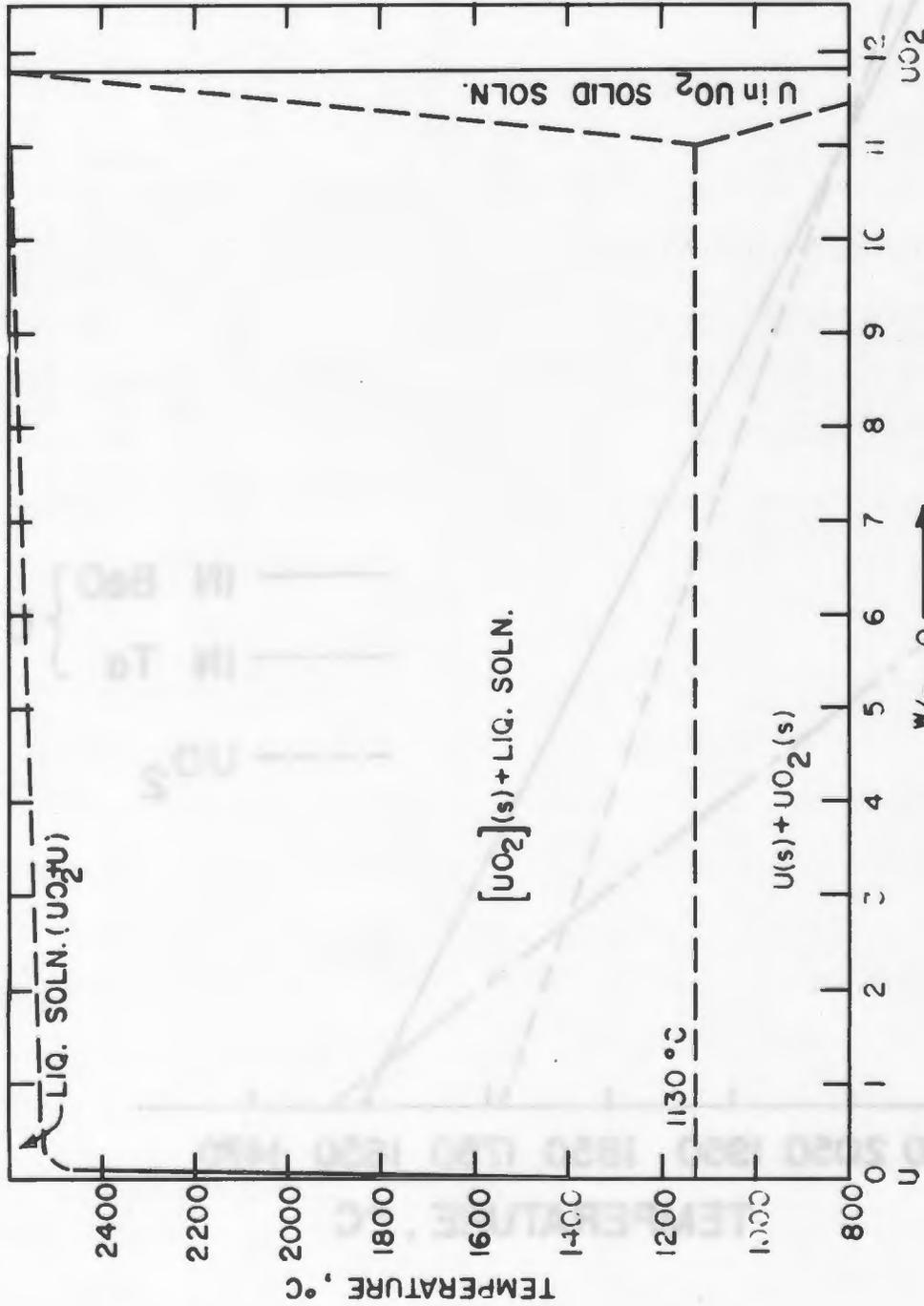


Fig. 7. Hypothetical diagram of U-UO₂ system.

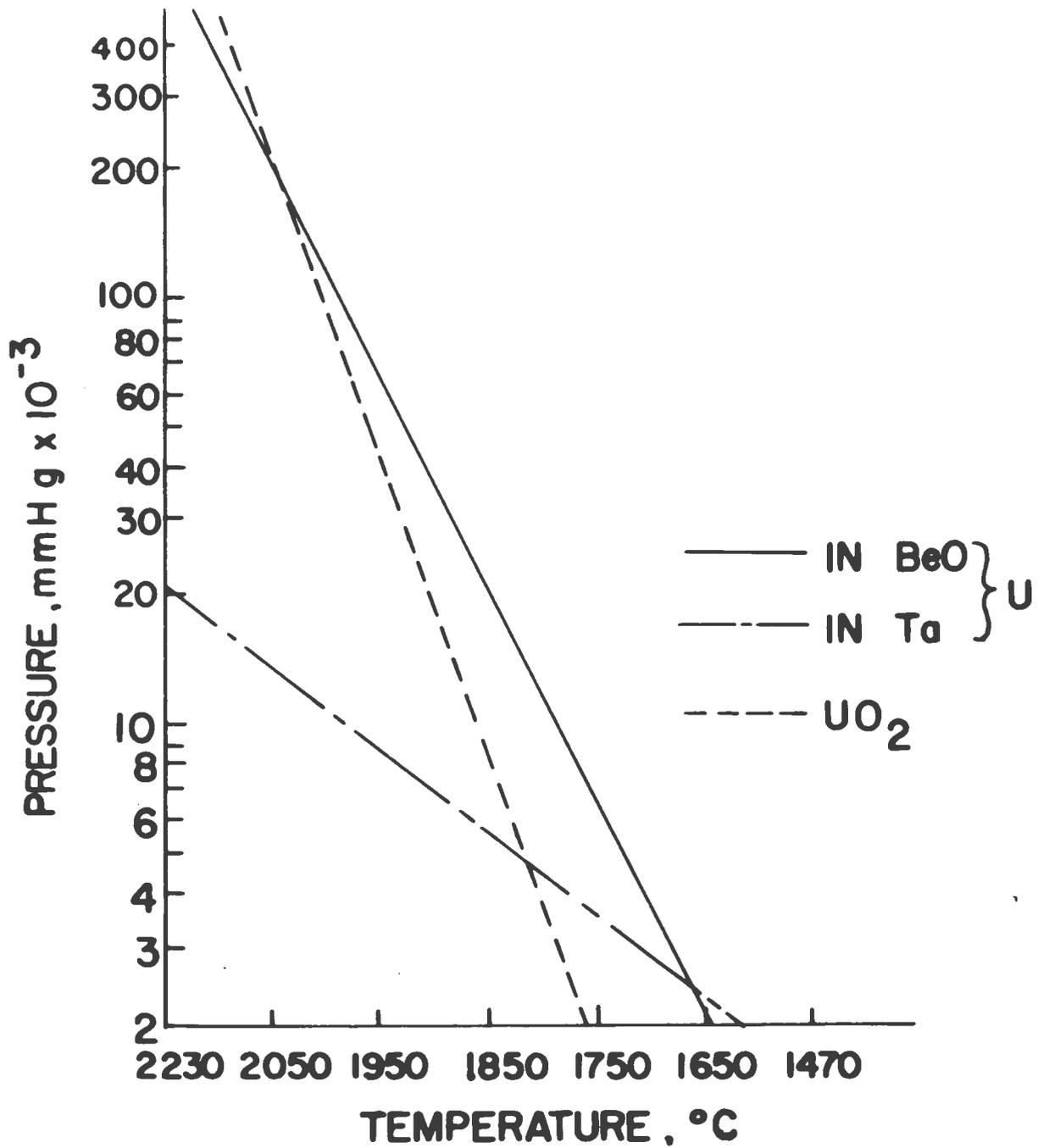


Fig. 8. Vapor pressures of U and UO₂ with temperature.

UO₂, that has sublimed out of the charge, reacting in actually colder areas of the graphite heating chamber. No data are available yet on these possibilities.

At the end of the heating program for such an experiment carried out successfully in a graphite crucible, the product is completely molten and has reacted with the crucible to form a solution of uranium carbide in uranium metal. The total weight of all residual uranium in this product, depends on the size of charge and heating program; this weight may be as low as 85% of the amount of uranium originally placed in the crucible as oxide. Volatility of uranium or uranium oxide or both at the high temperatures employed, no doubt, contributes to this loss of uranium. Data on the volatility of the carbide are not available.

It appears from consideration of the above that to obtain high yields of good metal by direct carbon reduction will require some new developments in container materials or in processing techniques or both. Sylvania employed graphite crucibles which reacted with the product to give metal high in carbide (about 50% UC). If the reaction could be carried to completion in an inert crucible material, then an objective of good quality metal in high yields might readily be realized. Sylvania gave this phase of the problem some attention and tested a few seemingly potential crucible materials without success. The main phases of the present effort on the carbon reduction of UO₂ at Ames are directed toward seeking a solution to or devising a new process to avoid the crucible problem.

For convenience in induction heating it is very desirable to retain the graphite heater employed in the setup as shown in Fig. 4. Such a simple arrangement for this process requires then that the crucible material holding the charge should be relatively inert to both molten uranium and graphite up to temperatures of about 2200°C. A more complex setup would be to employ a crucible base that is inert to both graphite and the crucible with the crucible being inert to uranium. Another approach would be to carry the reaction in a graphite crucible just to the stage where the charge becomes a sufficient conductor to be heated by self-induction, remove the charge from the graphite crucible, repack it in a properly insulated crucible inert to metal and then complete the reaction at the higher temperatures.

Some refractory oxides that are now receiving consideration in the fabrication of crucibles for use as containers to complete the reaction in graphite heaters include:

Urania	UO_2	
Thoria	ThO_2	
Zirconia	ZrO_2	
Yttria	Y_2O_3	and
Beryllia	BeO	.

The high vapor pressure of UO_2 , especially near the top temperature, renders this material unreliable since the crucible wall may deteriorate by vaporization and fail, thus letting the metal flow to the graphite heater. There is also a slow reaction between the graphite and the UO_2 crucible at their interface. The microstructure shown in Fig. 9

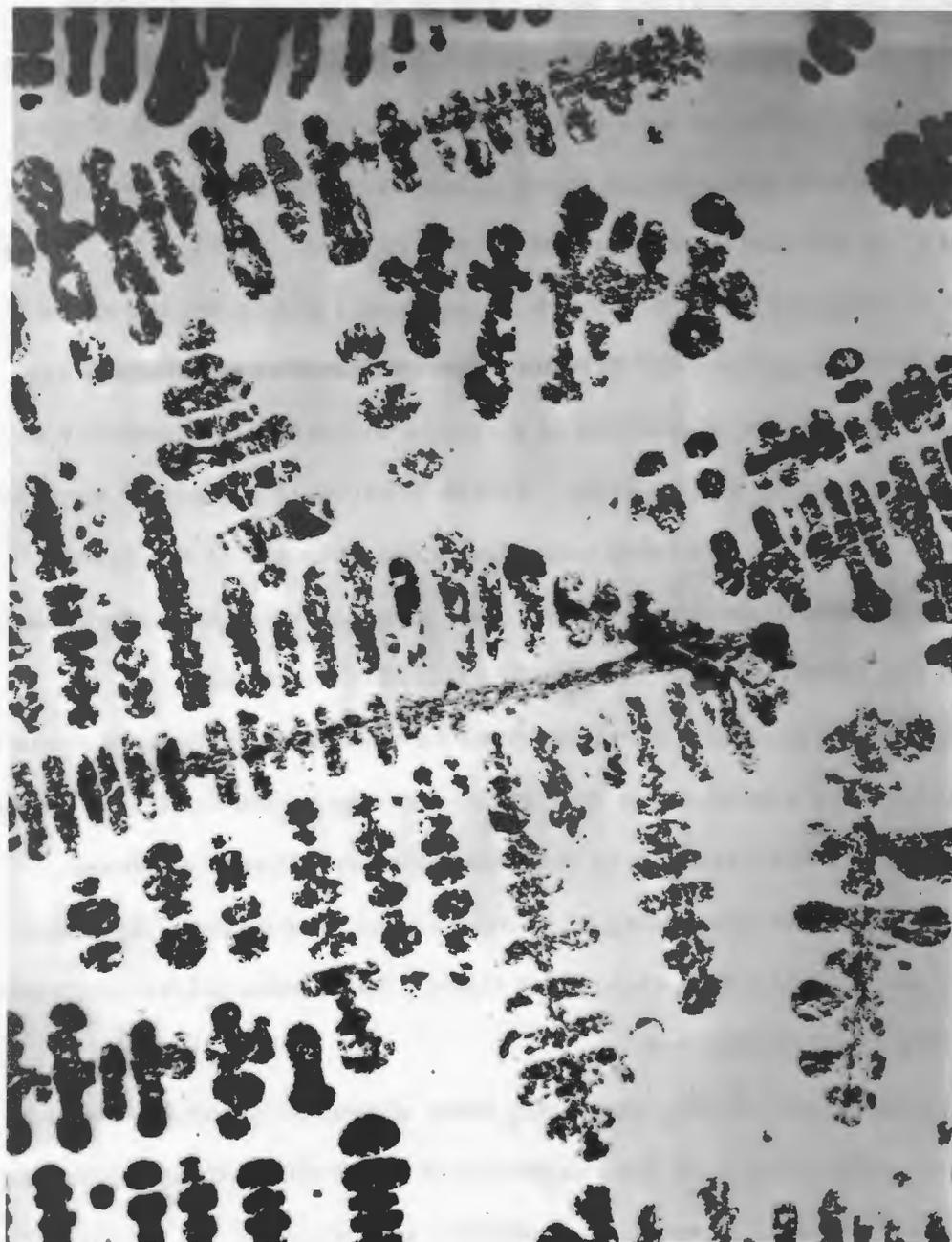


Fig. 9. Microstructure of uranium metal that has contacted graphite heater. Dark phase is UC dendrites. 100X.

is typical for metal that has been allowed to contact the graphite heater for a short time after crucible failure at the top temperature. One heating of a charge in a urania crucible was terminated just as the crucible wall approached paper thinness. The molten metal was still retained; a microstructure of this metal is shown in Fig. 10. Thoria seems to be fairly inert to a low-carbon metal phase but it reacts rapidly with the graphite. Zirconia was not used alone since large crucibles have to be of stabilized zirconia to lessen the tendency to fracture on heating and cooling. Yttria behaves in a manner similar to thoria. Beryllia has been considered but because of the toxicity ascribed to beryllium compounds it, as a major crucible constituent, has not yet been tested in this study on carbon reduction.

Except for possibly beryllia, none of the above materials alone is satisfactory for containing a charge where a graphite heater is employed to complete the reaction in the manner prescribed. However, ceramic crucibles consisting of combinations that include the above oxides, as well as a few others not listed, have been tested and some promising results obtained.

Combinations of UO_2 and ThO_2 have shown promise in that the volatility of the UO_2 and the reactivity of the ThO_2 with graphite are markedly reduced. However, problems still exist in the fabrication of good crucibles with these mixtures. Small additions of yttria and of zirconia to UO_2 - ThO_2 combinations have also given mixtures that show promise as crucible materials for the high temperature reaction. Yttria-stabilized zirconia crucibles appear resistant to the graphite

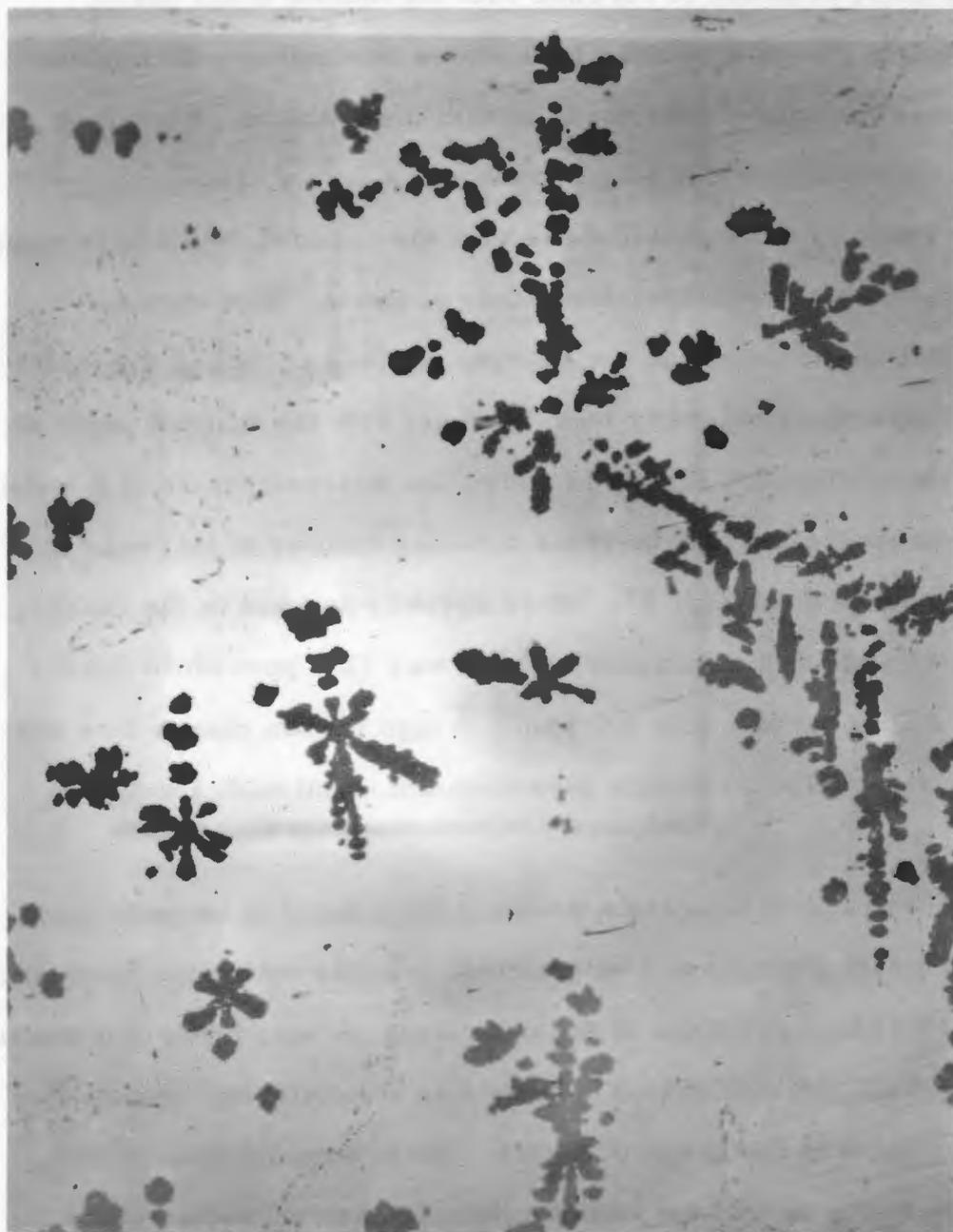


Fig. 10. Microstructure of uranium metal retained in urania crucible. 100X.

but show some evidence of reaction with the molten metal phase. Thoria-yttria (50-50) crucibles have shown only minor attack by the metal phase but appreciable reaction with the graphite. Figure 11 shows a microstructure of metal produced in such a crucible.

The reaction of the metal phase with the ceramic crucible in some cases, particularly with crucibles made of thoria, have shown a relationship to the carbon in the charge. Excess carbon in the metal at high temperature evidently tends to react with the thorium oxide of the crucible material. Figure 12 shows the microstructure of a sample of metal produced in a thoria-yttria crucible similar to that used to prepare the metal for Fig. 11. More carbon was used in the charge for Fig. 12 and the thorium pick up here was 1200 ppm while for the metal of Fig. 11 it was only 200 ppm. A high carbon charge that was heated in a pure ThO_2 crucible gave uranium metal with nearly 1 % thorium.

Some refractory materials that have been found to be quite inert to reaction with graphite and with certain crucible materials have been employed as bases for some of the crucibles. A base made of a mixture of $\text{UO}_2(56)\text{ThO}_2(26)$ and $\text{ZrO}_2(18)$ served as a satisfactory support for thoria crucibles in the graphite heater. Other combinations of UO_2 , ThO_2 with Y_2O_3 , as well as tantalum metal, have served as bases for ceramic crucibles that are subject to reaction with graphite.

It is to be noted that in all microstructures shown in figures referred to above, the carbide phase is present. Some work is being done on an approach designed to prepare a metal that contains excess



Fig. 11. Microstructure of uranium metal prepared in thoria-yttria crucible. Thorium in metal 200 ppm. 100X.



Fig. 12. Microstructure of metal prepared in thoria-yttria crucible. Charge with excess carbon. Thorium in metal 1200 ppm. 100X.

oxide with little or no carbide. The proposal then is to remove the residual oxygen from the uranium metal by subsequently heating it with calcium metal at a temperature just above the melting point of uranium. The small amount of calcium oxide formed here, it is hoped, would float on top of the uranium. The preparation of completely carbon-free metal in the present set up has not yet been attained, however. This may, in part, be due to the slight vapor pressure of carbon from the graphite heater at the upper temperatures. Exploration of the potentialities of electron-beam melting of some of the carbon reduced product containing small amounts of oxide, of carbide or of both will be tested as a means to complete the process for high-purity metal.

Possibly metal obtained by the carbon reduction of the oxide can be prepared sufficiently free of oxide and carbide to serve as anode material for electrolytic refining. This potentiality may be of immediate value in the preparation of small amounts of super-pure metal.

If one observes the microstructures of metal that can be readily prepared in some of the special ceramic crucibles, it may be noted that carbide, generally as long dendrites, appears to be the prevailing inclusion. Possibly because of this shape these less dense dendrites do not readily segregate near the top of the liquid metal phase as they crystallize from the liquid solution. If in a subsequent treatment these dendrites are granulated then, in molten uranium metal, they should tend to segregate as finer particles toward the top of the melt and leave essentially carbon-free uranium in the lower section of the melt.

The carbon rich section could be removed by cropping or possibly by hydrolysis and a massive low-carbon biscuit of uranium recovered. Although no attempt was made to promote such segregation, Fig. 13 shows a lower section of the metal ingot for which the average microstructure was shown in Fig. 11. The low carbide content here appears to be due to the less dense carbide rising toward the top of the liquid metal. There is some evidence that when there is a small amount of residual oxide in the metal, a tough network of the oxide tends to form throughout the liquid metal phase and thus prevents the desired segregation of the carbide. If such a network does form on cooling the metal from the high temperature, then some physical means for destroying the network might effectively promote the desired carbide segregation.



Fig. 13. Microstructure of low carbon region in uranium product due to segregation. Straight lines are scratches in soft metal. 100X.

BIBLIOGRAPHY

USAEC Rept. No. ISC-1076 (1960), Office of Technical Services,
Washington, D. C.

USAEC Rept. No. ANL-5750 (1957), Office of Technical Services,
Washington, D. C.

Notebook EPN-1 and -2, Document Library, Ames Laboratory,
USAEC, Ames, Iowa.

USAEC Rept. No. SCNC-241 (1957), Office of Technical Services,
Washington, D. C.

Bulletin 584, U. S. Bureau of Mines, Publications Distribution
Section, Pittsburgh, Pennsylvania.

Joseph J. Katz and Eugene Rabinowitch, The Chemistry of
Uranium, Part I. The Element, Its Binary and Related Compounds
(McGraw-Hill Book Co., Inc., New York, 1951).

John F. Elliott and Molly Gleiser, Thermochemistry for Steelmaking
(Addison-Wesley Pub. Co., Inc., Reading, Mass., 1960), Vol. I.