LA--11954-T

DE91 010893

LA-11954-T
Thesis

UC-504
Issued: April 1991

*Experimental Investigation of Uranium
Dicarbide Densification and the
Influence of Free Carbon Diffusion*

Kenneth Max Chidester

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGMENTS

The author would like to thank the Los Alamos National Laboratory and U. S. Department of Energy for providing funding for this research. Thanks for the opportunity to use an outstanding fuels development facility and equipment during the course of this investigation.

Gratitude is extended to Dr. R. Bruce Matthews for interactive discussions, support, and patience during the performance of this work.

The author would like to thank Professor Mohamed El-Genk for his encouragement and helpful discussion, which added greatly to the accomplishment of this work.

Thanks to Ed Storms for many valuable insights, tutoring, and discussions.

A special thanks goes to Gene Moore for his tireless effort in helping prepare, run, and measure samples throughout this investigation. Without his help, little would have been accomplished. Thanks to all the technicians in the Nuclear Fuels group who contributed much to this work.

The author is grateful to Nora Rink for her efforts in helping to prepare this manuscript.

Table of Contents

1.0	Introduction.....	1
2.0	Background.....	3
2.1	Techniques for Fabricating UC ₂	3
2.2	Sintering Theory.....	4
3.0	Experimental Techniques.....	5
3.1	Processing Equipment.....	5
3.2	Feed Powder Preparation.....	5
3.3	Sample Preparation and Testing.....	13
3.4	Characterization of Test Specimens.....	13
3.5	Feed Material.....	15
4.0	Introduction to Test Results.....	18
5.0	Test Results.....	19
5.1	Test to form high density UC ₂ compacts.....	19
5.2	Sintering Aid Tests.....	28
5.3	Tests Studying UC ₂ Densification on Refractory Metals with Time....	29
5.4	Tests Studying the Effect of Temperature on UC ₂ Densification.....	38
5.5	Variable C/U Composition and Time Tests.....	41
5.6	Tests on Molybdenum, Rhenium, and WC.....	49
5.7	Tests on Carbon Pickup in Tungsten Tray.....	49
5.8	Tests of Sintering Atmosphere.....	55
5.9	General Behavior Tests.....	59
5.10	Observations on Oxygen and Nitrogen Impurity Effects.....	61
5.11	Duplex Pellet Tests.....	62

Table of Contents (continued)

6.0	Analysis and Discussion.	66
6.1	Future Work.	77
7.0	Conclusions.	78
	Selected Bibliography.	79

List of Figures

3.1.1	Inert atmosphere glovebox with gas and vacuum equipment below.	6
3.1.2	Ball mill with quart jars.	7
3.1.3	Vibratory mill, tube filled with steel balls.	7
3.1.4	10-ton Carver hand press with punch-and-die set under pressure.	8
3.1.5	Inside view of high-temperature furnace loaded with UC _x pellets in graphite tray.	9
3.1.6	High temperature furnace control console.	10
3.2.1	Briquettes in a graphite tray inside furnace.	12
3.5.1	Phase diagram of the U-UC ₂ system.	17
3.5.2	Variation of carbon diffusion constant D at 2373 K in UC _x for varied C/U ratios.	17
5.1.1	UC ₂ pellet sintered at 2373 K for 3 h. Shiny end was in contact with tantalum and is high density.	22
5.1.2	Duplex density UC ₂ pellet sintered on tantalum for 3 hours at 2373 K. ...	23
5.1.3	Unetched, as-polished and etched micrographs of a sintered UC ₂ pellet from batch 5 sintered for 48 hours at 2373 K.	24
5.1.4	Photomicrograph of UC ₂ pellets (batch 5) sintered at 2373 K on tantalum .. for time indicated.	25
5.1.5	Photomicrograph of UC ₂ pellets (batch 5) sintered at 2373 K on tantalum for time indicated.	26
5.1.6	Partially sintered UC ₂ pellets from batch 5 exhibiting “directional zone sintering” from the surface in contact with tantalum.	27
5.1.7	Cross section of a partially sintered UC ₂ pellet sintered for 30 min at 2373 K in contact with tantalum metal on each end.	27
5.3.1	Directional zone sintering effects of UC ₂ on tungsten for various times. Time at sintering temperature and height of the densified region increases from left to right: (a) 600 sec, (b) 1200 sec, (c) 2400 sec, (d) 3600 sec, (e) 5400 sec, (f) 7200 sec, (g) 10,800 sec, (h) 14,400 sec, (i) 21,600 sec. 32	32

List of Figures (continued)

5.3.2	UC ₂ densification on tungsten, niobium, and tantalum with time at 2373 K.	32
5.3.3	UC ₂ densification on tungsten, niobium, and tantalum at 2273 K.	33
5.3.4	UC ₂ densification on tungsten with time at 2273 K.	33
5.3.5	UC ₂ densification on niobium with time at 2273 K.	34
5.3.6	UC ₂ densification on tantalum with time at 2273 K.	34
5.3.7	UC ₂ densification on tungsten with time at 2373 K.	35
5.3.8	UC ₂ densification on niobium with time at 2373 K.	35
5.3.9	UC ₂ densification on tantalum with time at 2373 K.	36
5.3.10	UC ₂ densification on tungsten with square root of time.	36
5.3.11	UC ₂ densification on niobium with square root of time.	37
5.3.12	UC ₂ densification on tantalum with square root of time.	37
5.4.1	Height of densified region vs temperature. Second order polynomial fit to each data set is shown.	39
5.4.2	Effect of temperature on densification rate.	42
5.5.1	Example schematic of a sliced UC ₂ pellet showing slice thickness and weight per cent carbon in each slice.	45
5.5.2	Weight per cent carbon from slices cut along axis of batch 5 UC ₂ pellets sintered at 2373 K for various times.	47
5.5.3	Weight per cent carbon from slices cut along axis of a batch 6 UC ₂ pellet sintered at 2373 K for 6 h.	47
5.5.4	Weight per cent carbon slices cut along axis of batch 7 UC ₂ pellets sintered at 2373 K for 3, 6, and 12 h.	48
5.6.1	Mo-U phase diagram.	50
5.6.2	Re-U phase diagram.	50

List of Figures (continued)

5.7.1	Tungsten carbide forming in a plate of tungsten metal. UC_2 pellet was located on top of tungsten carbide during sintering. Hardness indentations made with Vickers hardness tester.	52
5.7.2	Tungsten carbide forming in tungsten metal after (a) 4 h and (b) 8 h.	53
5.7.3	Tungsten carbide forming in tungsten metal after (a) 12 h and (b) 16 h. ...	53
5.7.4	Penetration depth of W_2C formed while sintering UC_2 on tungsten.	56
5.9.1	Schematic of high density regions of stacked UC_2 pellets on niobium after 6 hours at 2373 K.	60
5.11.1	Sintered duplex composition UC_x pellets. C/U for one end 1.95 and for the other, 1.50.	63
5.11.2	Photo of a partially sintered duplex composition pellet cut lengthwise and polished. Composition of high density end, C/U = 1.5, and low density end, C/U = 1.95.	63
5.11.3	Duplex composition pellet weight per cent carbon profile after sintering at 2373 K.	65
5.11.4	Weight per cent carbon values along the length of UC_2 duplex pellets, carbon content 7.04 wt% on one end (C/U = 1.50) and 9.46 wt% on the other (C/U = 2.07), sintered for 3, 6, and 12 h on WC at 2373 K.	65
6.0.1	Typical concentration profile for diffusion of material C across a chemical gradient between materials A and B682	
6.0.2	Plot of the measured height h of densified region with time and calculated values at different D values. On tungsten.	72
6.0.3	Measured vs calculated position of densified height with various D values. On tungsten.	72
6.0.4	Measured vs calculated position of densified height with various D values. On niobium.	73
6.0.5	Measured vs calculated position of densified height with various D values. On tantalum.	73
6.0.6	Comparison of measured and calculated carbon level at various distances from the pellet end. Sintered for 3 h at 2373 K.	76
6.0.7	Phase diagram of the U- UC_2 system. (Storms 1967).	76

List of Tables

3.5.1	Uranium Carbide Feed Batch Data.	15
5.1.1	Density of UC_x Compacts Sintered at 2373 K for 12 h.	19
5.1.2	Effect of Time at 2373 K on Density, Grain Size, and Composition.	20
5.2.1	Summary of Sintering Aid Addition Tests for UC_2	29
5.3.1	Melting Point for Tungsten, Niobium, and Tantalum and Their Respective Carbides.	30
5.3.2	Densified Height Data for UC_2 Sintered on Tungsten, Niobium, and Tantalum for Varying Times.	34
5.4.1	Densified Height on Tungsten, Niobium, and Tantalum with Temperature.	40
5.4.2	Directional Zone Sintering Activation Energy (Q) for UC_2 on Niobium, Tantalum, and Tungsten Trays, Calculated from Empirical Data, Figure 5.4.2.	41
5.5.1	Results of Variable C/U and Time Tests.	44
5.7.1	W_2C Formation Depth in Tungsten with Time.	51
5.8.1	Density Results of UC_x Pellets Sintered in Vacuum at 2373 K.	57
5.8.2	Results of UC_2 Sintering Tests in Hydrogen.	58
6.0.1	Effective Diffusion Coefficient for Carbon Diffusion in UC_2 and the Movement of Densified Region Through all UC_2 Pellets.	74
6.0.2	Estimated D_0 Values for UC_2 Sintering on Niobium, Tantalum, and Tungsten.	74
7.0.1	Summary of Directional Zone Sintering of UC_2 on Refractory Metal Substrates: Activation Energies and Diffusion Constants.	78

Experimental Investigation of Uranium Dicarbide Densification and the Influence of Free Carbon Diffusion

by

Kenneth Max Chidester

ABSTRACT

Because UC_2 fuel is being considered for space reactor applications, an investigation of process parameters and densification mechanisms for this fuel was conducted for the DOE. Uranium dicarbide feed powder was prepared by carbothermic reduction of uranium dicarbide and graphite at 2050 K in vacuum. Uranium dicarbide pellets were prepared by cold pressing at 110 MPa and sintering at 2370 K in contact with niobium, tantalum, or tungsten substrates in argon, argon-hydrogen, and vacuum atmospheres. Argon proved to be the most effective for sintering.

A high density front was observed to move through the pellets, starting from the pellet-metal substrate interface. The primary factor controlling this phenomenon is the diffusion of carbon from the uranium dicarbide pellet into the metal substrate. When the carbon level reduces so that no free carbon is present, rapid densification of the uranium dicarbide occurs. The movement of the high density front can be predicted with carbon diffusion equations using the error function. The activation energy for the high density front movement was determined to be -130 to -180 Kcal/mole. An effective diffusion coefficient for carbon diffusion in UC_2 and the movement of the densified region was measured at $8 \times 10^{-7} \text{ cm}^2/\text{s}$.

This technique can be used to control densification of uranium dicarbide and to control carbon level and grain size in sintered compacts. More information on the fundamental carbon transport mechanism is necessary for complete understanding of the phenomenon.

1.0 INTRODUCTION

Carbide fuels have been proposed in past years as the advanced LMFBR fuel because of some valuable attributes, such as high thermal conductivity, high fuel-atom metal density, and increased stability under most reactor conditions (Suzuki et.al 1982, Zope 1975, Matthews and Herbst 1983). More recently, advanced reactor designs, especially those developed for space applications, propose to use UC and UC₂ as potential fuels. Because space reactors operate at high temperature in order to reduce the radiator area, they require high temperature fuels such as uranium carbides for operation. Not only are carbide fuels stable at high temperature but they also have a high melting temperature, thereby minimizing potential corrosion attack on metal components (Alexander 1963, Resnick and Seigle 1966) while operating at high power density.

To minimize fuel swelling due to retention of fission gases such as xenon and krypton, fuel materials are fabricated with some porosity, hence have a lower density. The density requirements for most high temperature applications are typically greater than 95% theoretical density (TD) and require special techniques for fabrication. Work has been done to develop a viable process for fabricating high density UC fuel pellets, but very little has been reported on process techniques to fabricate high density UC₂ fuel compacts. Most of the work with UC₂ was done on a laboratory scale with arc melting (Storms 1963, Frost 1963). This technique is not practical for fabrication of large quantities both because it is difficult to produce a homogeneous blend with large batches and because high purity uranium feed powder is difficult and expensive to obtain.

An economical process that uses reduction of UO₂ by carbon and standard ceramic processing techniques to produce and fabricate UC₂ is desired. The use of standard ceramic processing techniques of milling, cold pressing, and high temperature sintering improve control of final product properties such as homogeneity and composition. Cold pressing and sintering enable maximum flexibility in forming the shape desired and controlling densification and grain growth. They also produce a homogeneous product with very little variation in composition and physical attributes between compacts of the same batch. Uranium dicarbide in the C/U composition range of 1.85 to 1.95 is of most interest because it is closest to single phase UC₂ and has a higher melting point than higher carbon compositions (Storms 1967, Imoto et al. 1964). The composition in this range which yields the highest sintering rate is of most interest.

The objective of this research is two fold: (1) identify parameters important to the fabrication of high density UC_2 compacts by cold pressing and sintering at high temperature, and (2) experimentally investigate the mechanism for densification of UC_2 compacts on substrates of graphite, tungsten carbide, and refractory metal, including W, Nb, Ta, Re, and Mo.

In the experiments, the UC_x samples are maintained in contact with the various substrates at given temperatures for various times. Effects of temperature and time on the progression of the densification front in the samples is determined. The activation energy of the densification process is determined, and the effective diffusion coefficient is also determined. The temperature in the experiments is varied from 2123 K to 2373 K, and the time at temperature from 10 minutes to 48 hours. The carbon composition is varied from 1.05 to 2.01 to investigate the effect of free carbon on densification. The term "directional zone sintering" is introduced to describe a phenomenon discovered in this study wherein UC_2 pellets rapidly densify from the end(s) in contact with carbide-forming refractory metals.

Other tests investigating the effect of vacuum, argon, and hydrogen environment on uranium carbide densification as well as to assess the effectiveness of Ni, Ta, and Nb metal powders as potential sintering aids are performed.

Following this introduction are five more sections which detail the important aspects of this investigation. Section 2.0 contains a background discussion of techniques for fabricating UC_2 , sintering theory, and diffusion theory. Section 3.0 contains details of fabrication, analytical, and testing techniques and procedures used in this investigation. Section 4.0, which is an introduction to the test results presented in Section 5.0, describes the primary objectives of the investigation and how they were accomplished in the experiments. Section 5.0 is divided into several subsections describing the tests and presenting the results. These results include the effect of composition (carbon level), sintering temperature, time at temperature, sintering tray composition, and furnace atmosphere during sintering on the sintering process. Some discussion is included, but the bulk of the discussion of results is presented in Section 6.0, followed by recommendations for future work. The final conclusions for this investigation are presented in Section 7.0.

2.0 BACKGROUND

2.1 Techniques for Fabricating UC₂

The most common method of making UC₂ has been blending uranium powder and graphite and heating them in an arc melter under purified helium or argon (Storms 1963). The resulting melt can be crushed, reshaped, and sintered to the desired size and density. Another method involves heating uranium metal in a hydrocarbon gas atmosphere such as methane to produce UC at low temperature (~925 K) and UC₂ if reacted at a higher temperature (~1173 K) (Kalish 1960).

The method chosen for this study is a third technique known as a carbothermic reduction method. This method is economically more attractive because it uses a universally available feed material of UO₂ powder and uses standard high temperature vacuum furnaces for heating (Taylor and McMurtry 1961, Matthews and Herbst 1983). It involves blending UO₂ and graphite powder, compacting to improve intimate contact and handling, and heating in vacuum to above 1775 K for sufficient time to remove oxygen. Oxygen is released by the formation of CO at higher temperature and removed from the material by the vacuum . Several have reported difficulty in achieving low oxygen with this technique (Stoops and Hamme 1962 and Frost 1963), but more recent work on UC by Matthews and Herbst (1983) showed that with proper care and equipment, the oxygen could be reduced to 360 ±95 ppm. Lindemer et al. (1969) reported that removal of oxygen from a spherical UO₂ particle is controlled by diffusion of oxygen through the UC₂ layer of the microsphere to the surface. Suzuki et al. (1982) added that the kinetics of the carbothermic synthesis of uranium carbides may be influenced by the characteristics of the UO₂ feed powder and shape of the compacts.

UC₂ particle fuel can be synthesized directly in the shape and size desired. Other shapes such as cylinders generally require further processing by pulverizing the synthesized compacts, reshaping by pressing (hot or cold) and heating at high temperature to densify. A more detailed discussion of the powder preparation, pressing, and sintering techniques used in this study is presented in Section 3.0, Experimental Techniques.

2.2 Sintering Theory

An as-formed powder compact is composed of many individual grains surrounded by a porosity of 40 to 60 vol%. To reduce porosity and thereby increase density and grain size, materials are heated to provide the energy. The driving force for this process is the reduction of surface free energy that occurs because of the elimination of solid vapor interfaces. A net decrease in free energy of about 1 cal/g occurs when sintering material with 1-micron particles (Kingery et al. 1976). Several mechanisms have been proposed for transport of the material during densification: (1) vaporization from one surface and subsequent condensation to another surface, (2) viscous flow, (3) surface diffusion, (4) grain boundary or lattice diffusion, (5) plastic deformation, or (6) a counter-diffusion of vacancies and atoms through the grains themselves.

Because of the high melting point of UC_2 , the most likely two mechanisms involved in densification of UC_2 are numbers 4 and 6 (above), which describe solid sintering by diffusion. For solid diffusion, materials are heated close to the solidus temperature (Van Vlack 1964). With sufficient time at a high enough temperature, the atoms exposed on the surface of the particles can move by diffusion so that they are in contact and only one interface is formed. The single interface formed is a grain boundary and has lower energy than the former two surfaces. As this process continues, densification occurs.

To enhance the densification and grain growth process and enable achieving high density and large grains in a short time at reduced temperatures, additives called sintering aids are sometimes used (Kingery et al. 1976, Kuczynski 1984). Sintering aids are materials which are compatible with the host materials and usually form a low melting phase at the grain boundaries of the host material. The liquid phase increases bulk material mobility, so that with the natural surface free energy driving forces present, the material moves to a more favorable geometry with less applied heat energy. If the same heat is applied, the process occurs more rapidly. The sintering aid most commonly used in UC is metallic nickel powder (Matthews and Herbst 1983).

3.0 EXPERIMENTAL TECHNIQUES

3.1 Processing Equipment

The following is a brief description of the process used to prepare the uranium carbide test samples:

3.1.1. High purity inert atmosphere gloveboxes, see Figure 3.1.1, contain a static argon atmosphere purified with a "Dri-Train" manufactured by Vacuum Atmospheres. The oxygen and moisture level was maintained below 10 ppm. Material was not processed when the oxygen or moisture level exceeded this limit.

3.1.2. Powder preparation was done with several pieces of equipment. A ball mill containing 1.27-cm-diam stainless steel balls was used to mix and mill each composition, see Figure 3.1.2. A jaw crusher was used to reduce the size of synthesized UC_x briquettes to minus 20 mesh and a vibratory mill filled with 1.27-cm-diam stainless steel balls was used to reduce the sample particle size to minus 250 mesh, see Figure 3.1.3.

3.1.3. A 10-ton Carver hand press was used to press the UC_x compacts, hereafter pellets, to their final shape, see Figure 3.1.4.

3.1.4. A high-temperature all metal furnace was used for all synthesis and sintering runs, see Figure 3.1.5. The furnace contains a tungsten mesh heating element, along with tungsten and molybdenum heat shields. The furnace uses two thermocouples made of 74% W - 26% Re and 95% W - 5% Re; one controls and records the operating temperature and the other serves as overtemperature control in case of emergency. The thermocouples read temperature to ± 5 degrees K, but the furnace controls the heat zone temperature to within ± 15 degrees K. The furnace can operate under vacuum, inert, or reducing atmosphere. The gas was purified by removing all oxygen in a chip furnace containing titanium chips and removing moisture with a molecular sieve. An automatic controller was used to set the time-temperature profile, see Figure 3.1.6.

3.2 Feed Powder Preparation

Uranium dioxide was the feed material available for this investigation. In order to convert to uranium carbide, the UO_2 was blended with carbon in the form of graphite and reacted at temperatures above 1800 K to remove the oxygen and form UC_x according to the following chemical equation:

Figure 3.1.1. Inert atmosphere glovebox with gas and vacuum equipment below.

Figure 3.1.2. Ball mill with quartz jars.

Figure 3.1.3. Vibratory mill, tube filled with steel balls.

Figure 3.1.4. Ten-ton Carver hand press with punch-and-die set under pressure.

Figure 3.1.5. Inside view of high-temperature furnace loaded with UC_x pellets in graphite tray.

Figure 3.1.6. High-temperature furnace control console.

The UC_x feed powder for all the experiments described herein was prepared in six successive steps:

3.2.1. The UO_2 powder and graphite powder was weighed to within 0.01 g for each mixture and hand blended first. The blend was then placed in a ball jar with the steel balls and milled for 16 hours. After milling, the powder was separated from the balls by pouring the contents onto a sieve and collecting the powder in a pan below.

3.2.2. The UO_2 -graphite blend was pressed into 1.91-cm-diam briquettes for the synthesis process.

3.2.3. After briquetting, the material was loaded into a graphite tray, see Figure 3.2.1, and loaded into the high temperature furnace for synthesis by carbothermic reduction. The first step in this synthesis process was to establish a vacuum of approximately 5×10^{-5} torr. The furnace was then heated to a temperature between 1875 and 2150 K in 15 minutes. The furnace was held at the specified temperature for at least 4 hours to allow sufficient time for carbon to remove the oxygen as CO and form the appropriate carbide depending on the amount of carbon (graphite) added. After the hold at temperature, the furnace was cooled rapidly to room temperature.

3.2.4. One of the steps in reducing the UC_x briquettes to powder was crushing by putting the material through the jaw crusher until it all passed through a 16-mesh screen.

3.2.5. After crushing, a binder and lubricant in powder form were added to the crushed material. The purpose of these additives was to hold the particles together after pressing and enable the pellets to be extruded from the die cavity without scoring the die walls (uranium carbide powder is very abrasive). Experience lead to the addition of 0.3 wt% polyethylene glycol as a binder and 0.3 wt% stearic acid as the lubricant.

3.2.6. In order to press into a strong green (unfired) pellet and densify to high density, the crushed material was milled to a fine powder. This was accomplished by putting it through a vibratory mill and recycling the crushed material until all the powder passed through a 250-mesh sieve. The powder was fed in one end and proceeded through the mill tube where the stainless steel balls pulverized it to smaller and smaller particles. The total residence time was about 20 minutes for each pass. After the milling was completed the powder was stored in a special container sealed with an O-ring until use in each subsequent test.

Figure 3.2.1. Briquettes in a graphite tray inside furnace.

3.3 Sample Preparation and Testing

3.3.1. The first step in the preparation of test specimens was to press (compress) the test powder into the desired shape. This was done by loading around 2.0 grams of UC_x powder into a die cavity, inserting the punches and applying enough pressure (approximately 110 MPa) to form the pellet. During this step the density increased to 55% to 58% TD, and the specimens had enough strength to be handled and loaded into the furnace.

3.3.2. The specimens were then loaded into the furnace on the desired tray material and the desired atmosphere was established. The first part of the furnace program was designed to remove the binder and lubricant additives. The furnace was heated to 725 K in 1 hour and held at this temperature for 1 hour. The temperature was then increased rapidly to reach the sintering temperature of choice in 1 hour. The furnace was then held at this temperature for the desired time and cooled to room temperature in about 2 hours.

3.4 Characterization of Test Specimens

After each heating test was completed, measurements of diameter and height of densified zone were made and samples were submitted for analysis of carbon, oxygen, and nitrogen. Some pellets were measured for length and weight so the density could be calculated.

3.4.1. Immediately after each sintering run, a visual examination was done to see which of the test specimens showed directional zone sintering, reaction with the tray material, densification, and any other behavior anomalies, such as cracking, melting, etc.

3.4.2. The next step was mensuration of the specimens. The height of the densified zone was measured with a hand-held micrometer by holding the stationary end of the micrometer at the dense end of the pellet and moving the adjustable end until it was parallel with the top of the transition zone between high and low density. The accuracy of the measurement is within 0.003 inches or 76.2 microns, and the precision of the micrometer is about 0.0001 inch or 2.5 microns. The pellet diameter and length were also measured with a hand held micrometer. The weight was measured on an electronic balance to 0.001 gram. From these values the density was calculated in units of grams/cubic-centimeter and converted to percent of theoretical density by dividing by the theoretical density found in the literature. The uncertainty in densities calculated was estimated to be $\pm 0.20\%$ TD.

3.4.3. To verify phase composition, several powder samples from synthesized and sintered material were analyzed with an x-ray diffractometer.

3.4.4. The composition and impurity levels were determined by analytical chemistry techniques. Carbon was determined by heating crushed samples in a Leco WR-112 instrument. The carbon was reacted with oxygen to form CO, which was then converted to CO₂ and measured by a gas thermoconductivity cell. The instrument was calibrated with standards before each set of analysis. Oxygen and nitrogen impurity level was determined in a Leco LC-136 instrument. A crushed sample was melted with a nickel flux and reacted with graphite to release oxygen as CO which was then converted to CO₂ and measured by infrared analysis. Nitrogen gas was released during the heat and measured in a thermoconductivity cell. This instrument was also calibrated with standards. Standards were continually measured during this investigation and the accuracy for each type analysis follows:

Carbon analysis - 0.004 wt% (absolute)

Oxygen analysis - 0.0002 wt% (absolute)

Nitrogen analysis - 0.0002 wt% (absolute)

3.4.5. Many samples were submitted to metallography where they were sliced in half and polished for examination. To observe and measure grain size, the polished cross sections were etched to bring out the grain boundaries, using a mixture of equal parts of nitric acid, acetic acid, and water. The grain size measurements were done at a magnification of 500x. The lineal intercept technique (ASTM standard E112-77) was used to measure grain size. The hardness check was done with a Leitz microhardness tester for a Vickers hardness measurement.

3.4.6 To determine the carbon composition at positions along the length of the pellet sample, pellets were glued to a metal plug and sliced with a diamond saw. Generally, the porous end was glued to the plug and slicing began on the dense end first. After trial and error, a technique was developed using a small diameter (5 cm) blade. The first cut was taken approximately 0.064 cm from the high density end of the pellet. The second and subsequent cuts were taken at approximate intervals of 0.064 cm so the actual slices were approximately 0.036-cm thick. The thicknesses and actual positions of the cuts were not exact because of the vibration and wiggling of the saw blade and cuts on the low density end often had to be 0.003- to 0.006-cm thicker because they would tend to crumble. The actual position of a single cut could be off as much as 0.05 cm.

3.5 Feed Material

3.5.1. Uranium dioxide powder.

Lot: 0907

Weight% Uranium = 87.78

Particle size: 100 % -325 mesh (typically 5 to 10 microns)

The following impurities were above the detectable limits of the inductively coupled plasma (ICP) mass spectrometry:

Cadmium - 1 ppm

Iron - 30 ppm

Lead - 7 ppm

Tungsten - 290 ppm

Zinc - 2 ppm

Zirconium - 1 ppm

Calcium - 60 ppm

3.5.2. Graphite powder.

Lot: 1249

Weight% Carbon = 100.0

Particle size: 99 % -325 mesh

The following impurities were above the detectable limits of the ICP mass spectrometry:

Barium - 73 ppm

Calcium - 43 ppm

Iron - 4 ppm

Selenium - 6 ppm

Silicon - 20 ppm

3.5.3 With the above feed material, several batches of differing compositions (C/U ratios) were blended and synthesized to the carbide state. A summary of the basic carbon level for each test batch is contained in Table 3.5.1. These batches were used throughout this investigation.

Table 3.5.1. Uranium Carbide Feed Batch Data

<u>Batch</u>	<u>%U</u>	<u>C/U</u>	<u>Phase(s) at Rm Temp</u>
1	5.03	1.05	UC + U ₂ C ₃
2	6.10	1.30	UC + U ₂ C ₃
3	7.04	1.50	U ₂ C ₃
4	8.66	1.88	UC ₂ + UC
5	8.96	1.95	UC ₂ + C (free carbon)
6	9.21	2.01	UC ₂ + C (free carbon)
7	9.46	2.07	UC ₂ + C (free carbon)

Batch 1 was chosen because its composition represents the low end of the solid UC_x range (see Figure 3.5.1), and according to Wallace et al. (1968), this composition has a high carbon diffusion coefficient at sintering temperatures used in this investigation. According to the phase diagram presented by Storms (1967), the composition of batch 1 is a solid solution of cubic UC and cubic UC_{2-x} at the sintering temperature of 2100 C (2373 K). Upon cooldown to room temperature, it changes to UC and U_2C_3 .

Batch 2 composition is just over midway between UC and U_2C_3 . The same phases are present at 2100 C and room temperature as in batch 1, but the diffusion coefficient is lower. Batch 3 was chosen because its composition represents a single phase region of U_2C_3 , and it also has a low carbon diffusion coefficient.

Since it was expected that some carbon would leave during the sintering process, several compositions covering the range of interest were chosen. Batches 4 to 7 represent the compositions of real interest in this investigation. The composition of batch 4 is the highest melting of the compositions at the UC_2 -rich end of the single-phase region at the sintering temperature of 2100 C. The compositions of batches 5, 6, and 7 are in the $UC_2 + C$ region at 2100 C. All four of these compositions are cubic at 2100 C. On cooling to room temperature, batch 4 composition transforms to tetragonal $UC_2 + UC$, if cooled rapidly. In order to convert to $U_2C_3 + C$ as shown in the phase diagram, the material must be cooled slowly to allow time for the transition. Batch 5, 6, and 7 compositions are cubic $UC_2 + C$ at 2100 C and transform to tetragonal $UC_2 + C$ at room temperature, if cooled rapidly. Also, the carbon diffusion coefficient calculated from the data presented by Wallace et al. (1968) over the composition of C/U equal to 1.70 to 1.90 changes significantly, see Figure 3.5.2. If sintering of these compositions has some dependence on the diffusion of carbon, then the sintering rate is expected to follow the same trend as the diffusion coefficient.

Figure 3.5.1. Phase diagram of the U-UC₂ system. (Storms 1967)

Figure 3.5.2. Variation of carbon diffusion coefficient D at 2373 K in UC_x for varied C/U ratios (Calculated with constants presented by Wallace et al. 1968).

4.0 INTRODUCTION TO TEST RESULTS

The critical tests and experiments of this work were designed to accomplish three primary goals: (1) to fabricate high-density, large-grain uranium dicarbide compacts, (2) to define the parameters required to achieve high-density, large-grain uranium dicarbide, and (3) to define a possible mechanism for densification of uranium dicarbide. Very little work has been done with uranium dicarbide, especially on viable processing techniques, so the initial work for this study concerned doing basic cold press and sintering tests. The key parameters of temperature, time, atmosphere, sintering tray material, and carbon level were varied to help define parameters and provide clues to a sintering mechanism.

Once the key parameters were tested the work broadened to look at possible sintering aids to enhance densification and reduce sintering temperature. Since very effective sintering aids have been identified for uranium monocarbide, it was hoped that some would work equally well for uranium dicarbide.

By far the bulk of the experimental work focused on achieving the third goal of defining a uranium dicarbide sintering mechanism. The initial sintering parameter tests provided valuable insights into potential mechanisms for sintering. Heats at short times showed a high-density region sweeping through the compacts from an outer surface in contact with a refractory metal. These results focused the remaining experiments on carbon and refractory metal diffusion in uranium dicarbide and what role they play in the sintering process. While diffusion studies typically use tracer elements to indicate the rate of movement of one species through host matrix, this study looks at the growth rate of the high-density region at various times and temperatures. The rate of this densification was then used to calculate a process activation energy and diffusion rate, which was compared to carbon and metal diffusion rates reported in the literature. The species controlling densification rate was identified from reported diffusion data and confirmed experimentally.

5.0 TEST RESULTS

5.1 Test to Form High Density UC₂ Compacts

Right cylindrical pellets were prepared from the four powder batches with highest C/U by pressing in the Carver hand press. The green density of each pellet was ~ 57.5% TD. Some pellets were placed on tantalum or tungsten trays and others were placed on graphite. The pellets were then heated to 2373 K for 12 hours under an argon atmosphere. The pellets heated on tantalum or tungsten achieved the highest density, with batches 4 and 5 reaching a density of greater than 97% TD, see Table 5.1.1. Batch 6 reached a density of only 93.65 TD, probably because of the higher carbon content.

Table 5.1.1. Density of UC_x Compacts Sintered at 2373 K for 12 h

Batch No.	Starting Value x (C/U)	Sintered on Metal		Sintered on Graphite	
		Ending Value x (C/U)	Density (%TD)	Ending Value x (C/U)	Density (%TD)
4	1.88	1.74	97.7	--	96 ^a
5	1.95	1.78	97.5	--	90 ^a
6	2.01	1.87	93.6	--	73.7
7	2.07	1.94	65.6		

^a Pellets stuck to graphite tray. Density was estimated from sintered diameter.

The density of batch 7 was only 65.5% TD, which is just above the pressed green density. This behavior is similar to that reported by Imoto et al. (1963), where above a C/U ratio of 1.90 the sintered density achievable is greatly reduced, albeit they sintered in a vacuum atmosphere. Batch 4 achieved the highest density on the graphite tray of about 96% TD. Note that the densities for the batches 4, 5, and 6 pellets were estimated based on sintered diameter measurements only, because they stuck to the graphite tray and were chipped while being removed. There was a dramatic drop in sintered density when the C/U ratio of the starting batch was above 1.95 for the pellets sintered on graphite.

A sample pellet from each batch were crushed and analyzed for phase content by x-ray diffraction. Batch 4 (C/U = 1.74) was 90% tetragonal UC₂ and the balance cubic UC. Batches 5, 6, and 7 were 97% to 98% tetragonal UC₂ and the balance cubic UC.

It appears from these limited data, that the highest density can be achieved with a C/U ratio of 1.95 or below and sintering on a refractory metal tray. The increased density achieved on metal trays is the subject of several tests discussed in subsequent sections. The 1.95 C/U limit is convenient because other workers have reported that the highest C/U ratio for the α -phase UC_2 is 1.94 at room temperature if quenched from high temperature and little free carbon is present (Storms 1967, Imoto 1963). If, however, $UC_{1.94}$ is cooled slowly as done in these experiments, UC will precipitate out at lower temperatures and the dicarbide phase will be $UC_{1.86}$. The bulk of this work was done using the composition of batch 5, Table 3.1, because its composition is closest to the ideal single phase region and it exhibited excellent sintering behavior.

One disturbing thing revealed by these 12-hour sintering tests is the significant carbon loss that occurs. The C/U ratios reduced by as much as 0.17 during sintering because of vaporization of carbon to the furnace atmosphere and diffusion of carbon into the metal substrates. It can be concluded at this point that 12 hours is too long to hold UC_2 compacts at sintering temperatures if high C/U is desired.

To optimize densification and grain size with time, a series of sintering tests was run at 2373 K for times ranging from 3 to 48 hours. The results indicate that complete densification occurred as early as 4.5 hours, see Table 5.1.2. Increasing time had very

Table 5.1.2. Effect of Time at 2373 K on Density, Grain Size, and Composition

Time (h)	Density (% TD)	Grain Size (μm)	C/U
3	$\sim 87.5^a$	31^b	1.81
4.5	96.0	--	1.80
6	96.0	23	1.73
12	96.6	--	1.74
12	95.4	36	--
24	97.7	28	1.70
48	98.1	37	1.80

^a Densified on one end of pellet.

^b Grain size of high-density end; low-density-region grain size $< 10 \mu m$.

little effect on grain size, indicating that most of the grain growth occurred during the initial densification. The carbon level continued to decrease with time, as expected. The carbon loss correlates with the appearance of the gold color of tantalum carbide in each location where a pellet sat during the sintering runs. The pellet sintered for 3 hours was

not completely sintered, as seen by the density. The pellet did not sinter uniformly as expected, but a dense region grew from the end in contact with the tantalum (Figure 5.1.1). A polished and etched cross section of the pellet revealed a duplex density pellet (Figure 5.1.2). Based on the porosity, the high density end of the pellet appears to be over 95% TD, while the low density end is probably less than 80% TD. Even with this tremendous change in density over such a short distance, no stress is evident in the structure. The mobility of uranium and carbon must be very high in this transition region to enable movement of porosity out of the structure as grains are grown and not set up high stress between the high and low density areas. The striped grain structure seen in these samples matches the structure reported by others as UC_2 in the light phase and UC in the dark stripes (Imoto et al. 1963, Eyre and Sole 1963, and Magnier et al. 1963).

Confirmation of the phases was made on later samples by x-ray diffraction.

The etched structure seen in the pellet held for 48 hours is nearly identical to that seen in the high density end of the pellet held for only 3 hours (see Figure 5.1.3). Micrographs of pellets sintered for 3, 12, 24, and 48 hours are presented in Figures 5.1.4 and 5.1.5. The only difference appears to be a slight decrease in porosity after the longer soak time. This unusual zone sintering has not been reported in the literature and may help identify sintering mechanisms for UC_2 . Since it initiates from the end in contact with metal and proceeds through the rest of the pellet, it is called "directional zone sintering."

To see if directional zone sintering could be initiated at any point in contact with tantalum regardless of position on the pellet, four UC_2 pellets from batch 5 were heated to 2373 K for 1 hour in an argon atmosphere. The results are seen in Figure 5.1.6. Two pellets, (a) and (b), sat upright on tantalum, and (b) also had a piece of tantalum on the upper end. Pellet (c) sat on its side in contact with the tantalum tray, and pellet (d) sat on graphite. Note that every part in contact with tantalum sintered rapidly from the point of contact. Also note that the pellet on graphite sintered much less than the other pellets. The shiny ends of pellets (a) and (b) was 0.04 cm smaller in diameter than the dull low-density end. From this test, it is evident that densification will occur from any point in contact with tantalum metal. The (b) pellet shown in Figure 5.1.6 was cut lengthwise, then mounted and polished for examination. It was evident from the cross section that the pellet was densifying from each end in contact with the tantalum metal, see Figure 5.1.7, and a high density front was moving through the pellet from each end.

At least three possible mechanisms exist for this behavior: (1) the carbon is leaving the UC_2 pellet, due to the chemical gradient, to form a carbide with the tantalum, thereby

Figure 5.1.1 UC pellet sintered at 2373 K for 3 h. Shiny end was in contact with tantalum and is high density.

Figure 5.1.2. Duplex density UC_2 pellet sintered on tantalum for 3 h at 2373 K.

As-polished, 95% T.D. 250x

Etched, 95% T.D. 500x

Figure 5.1.3. Unetched as-polished and etched micrographs of a sintered UC₂ pellet from batch 5 sintered for 48 h at 2373 K.

3h, grain size = $30.8\mu\text{m}$

500X

12h, grain size = $36.1\mu\text{m}$

500X

Figure 5.1.4. Photomicrographs of UC_2 pellets (batch 5) sintered at 2373 K on tantalum for time indicated.

24h, grain size = 27.7 μm

500X

48h, grain size = 36.9 μm

500X

Figure 5.1.5. Photomicrograph of UC_2 pellets (batch 5) sintered at 2373 K on tantalum for time indicated.

Figure 5.1.6. Partially sintered UC_2 pellets from batch 5 exhibiting “directional zone sintering” from the surface in contact with tantalum.

Figure 5.1.7. Cross section of a partially sintered UC_2 pellet sintered for 30 min at 2373 K in contact with tantalum metal on each end.

increasing the carbon mobility and enhancing material movement during densification, and/or (2) tantalum atoms may be diffusing into the uranium carbide and function as a sintering aid, or (3) an impurity such as oxygen may form a low melting compound or enhance uranium dicarbide phase transition to the cubic phase at the sintering temperature. The balance of tests reported herein focus on understanding and verifying one or more of these possibilities.

5.2 Sintering Aid Tests

Sintering aids are commonly used to enhance densification of nonmetallic materials and reduce the temperature required (Kuczynski 1984). The most common sintering aids are metals or nonmetals that melt at low temperature and wet the grain boundaries, but do not chemically react with the host material. Powdered nickel has been successfully used as a sintering aid for UC. Densities up to 97% TD are achieved with an addition of 2000 ppm nickel and a temperature of 1873 K (Matthews and Herbst 1983, Pickels et.al 1980). To test the effectiveness of nickel, tantalum, and niobium as sintering aids for UC₂, different amounts of these metal powders were added during the milling process. Pellets were pressed and sintered at different temperatures. The tests showed that none of these metals improved sintering of UC₂ at all, see Table 5.2.1.

To determine how much metal is diffusing into the UC₂ pellets that exhibit directional zone sintering, a long pellet (1.25 cm.) was sintered on tungsten until the high density region was about 50% of the pellet length. The pellet was then cut into thirds and submitted for tungsten impurity analysis using chemical dissolution and color spectrophotometric determination. The analysis showed 40-ppm tungsten in the high density region, 35-ppm tungsten in the center region, and none detectable in the low density region. Since only 40 ppm was found in this test, another test was run with UC₂ powder doped with 50-ppm and 100-ppm niobium and pressed into pellets. The pellets were sintered, one each on niobium, tungsten, graphite, and WC, first for 1 hour and then for another 2 hours. The pellets sintered on WC and graphite were dull in appearance and only sintered to a density of 80% TD. The pellets sintered on the niobium and tungsten behaved typically with a high density region growing from the end in contact with the metals. After the two-hour heat, these two pellets were completely sintered to a density of 94.8% TD. It appears from these tests that niobium, nickel, and tantalum are not effective sintering aids for UC₂ when added and blended into the UC₂ powder. They also do not interfere with directional zone sintering when added in quantities up to 2000

ppm. It is still possible, however, that zone sintering is dependent on refractory metal atoms diffusing into the UC_2 and interacting with oxygen contaminants at the diffusion front to form low melting oxides and enhance material mobility. Further testing of this possibility appears in subsequent Sections 5.10 and 5.11.

Table 5.2.1. Summary of Sintering Aid Addition Tests for UC_2

Test	Sintering Aid	Amount (ppm)	Temp / Time (K / h)	Holding Tray Material	Density (%TD)	
1.	Ni	2000	1825 / 1	Graphite	50.0	
2.	Ni	2000	2373 / 12	Ta	90.5	
3.	Ta	200	2373 / 6	Graphite	63.0	
4.	Ta	500	2373 / 6	Graphite	62.8	
5.	Ta	1000	2373 / 6	Graphite	62.5	
6.	Ta	2000	2373 / 6	Graphite	63.3	
7.	Ta	200	2373 / 2	Ta	74.5*	
8.	Ta	500	2373 / 2	Ta	73.6*	
9.	Ta	2000	2373 / 2	Ta	74.2*	
10.	Nb	50	2373 / 1 & 2.25	Nb	*	94.2
11.	Nb	50	2373 / 1 & 2.25	W	*	94.7
12.	Nb	50	2373 / 1 & 2.25	WC	78.4	80.6
13.	Nb	50	2373 / 1 & 2.25	C	77.2	79.7
14.	Nb	100	2373 / 1 & 2.25	Nb	*	94.3
15.	Nb	100	2373 / 1 & 2.25	W	*	95.2
16.	Nb	100	2373 / 1 & 2.25	WC	77.4	80.2
17.	Nb	100	2373 / 1 & 2.25	C	76.0	78.1

*Each of these pellets exhibited zone sintering with high density region about 0.254-cm high.

5.3 Tests Studying UC_2 Densification on Refractory Metals with Time

Since tungsten and niobium are refractory metals and carbide formers like tantalum, they were also chosen to hold UC_2 samples during sintering tests. The melting temperature of the three metals and their respective carbides vary by as much as 1000 K (see Table 5.3.1), so if they act as sintering aids in UC_2 , their effects should differ dramatically also. If they simply act as a carbon sink, their effect on UC_2 sintering should be dependent on carbon diffusion in the metal and their respective carbides.

Table 5.3.1. Melting Point for Tungsten, Niobium, and Tantalum and Their Respective Carbides

Material	Melting Points (K)	Reference
Tungsten	3685	CRC ^a
Niobium	2740	CRC
Tantalum	3270	CRC
W ₂ C	3155	CRC
WC	3145	CRC
NbC	3775	CRC
Nb ₂ C	3365	Storms and Krikorian 1960
Ta ₂ C	3675	Ellinger 1943
TaC	4155	CRC

^a CRC Handbook of Chemistry and Physics, 4th Ed., 1983.

A series of tests was done with UC₂ pellets heated while sitting on one of the three metals tungsten, niobium, or tantalum at 2373 K for various times. These tests were repeated at 2273 K for various times. To assure consistency between test heats, fresh pellets and new pieces of metal were used each time. The height of the densified region varied with time for each of the metals used and can be easily seen visually because the high density region has a very shiny appearance and the low density region appears dark and lackluster (see Figure 5.3.1). The height was measured with a hand-held micrometer from the end in contact with the refractory metal to the top of the transition zone. The height was measured in mils and converted to centimeters for convenience of calculating. The values obtained at 2273 and 2373 K are seen in Table 5.3.2.

The most convenient way to observe the effect of this zone sintering growth is to look at a plot of the densified height vs time. Figure 5.3.2 contains the results for all three metals at 2373 K, and the results for the heats at 2273 K can be seen in Figure 5.3.3. The plots for each individual metal are found in Figures 5.3.4-5.3.9. The behavior appears to follow a parabolic relationship with time on each metal. Borg and Dienes (1988) and Kofstad (1988) suggest that this means the densification growth is diffusion dependent on a single diffusing species. Further verification of this can be seen by plotting the same height vs $\sqrt{t}$ for each metal used. Example plots for UC₂ sintered on tungsten at 2273 K and 2373 K are seen in Figure 5.3.10. Note that the slope reduces with the change in temperature, indicating a direct dependency on temperature. The plots of results on Nb and tantalum are found in Figures 5.3.11 and 5.3.12. The software used to plot these data includes a curve-fitting program that uses a least squares approach to fit the data to a

Table 5.3.2. Densified Height Data for UC₂ Sintered on Tungsten, Niobium, and Tantalum for Varying Times

Temp (K)	Time (sec)	Height of Densified Region		
		W	Nb (cm)	Ta
2373	600	0.064	0.064	0.064
	1200	0.102	0.102	0.089
	2400	0.160	0.152	0.114
	3600	0.191	0.178	0.127
	5400	0.229	0.203	0.178
	7200	0.279	0.279	--
	10800	0.318	0.320	0.269
	14400	0.389	0.406	0.381
	21600	0.483	--	0.445
	36000	0.681	0.851	--
2273	600	0.041	0.062	0.036
	1200	0.094	0.089	0.086
	1800	0.099	0.107	0.072
	2400	0.112	0.104	0.079
	3600	0.152	0.153	0.114
	5400	0.224	0.239	0.178
	10800	0.241	0.267	0.229
	18000	0.489	0.462	0.379
	24000	0.445	0.546	0.356
	30000	0.546	0.533	0.394
	36000	0.470	0.572	0.521

Figure 5.3.1. Directional zone sintering effects of UC_2 on tungsten for various times. Time at sintering temperature and height of the densified region increases from left to right: (a) 600 sec, (b) 1200 sec, (c) 2400 sec, (d) 3600 sec, (e) 5400 sec, (f) 7200 sec, (g) 10,800 sec, (h) 14,400 sec, (i) 21,600 sec.

Figure 5.3.2. UC_2 densification on tungsten, niobium, and tantalum with time at 2373 K.

Figure 5.3.3. UC_2 densification on tungsten, niobium, and tantalum at 2273 K.

Figure 5.3.4. UC_2 densification on tungsten with time at 2273 K.

Figure 5.3.5. UC_2 densification on niobium with time at 2273 K.

Figure 5.3.6. UC_2 densification on tantalum with time at 2273 K.

Figure 5.3.7. UC₂ densification on tungsten with time at 2373 K.

Figure 5.3.8. UC₂ densification on niobium with time at 2373 K.

Figure 5.3.9. UC₂ densification on tantalum with time at 2373 K.

Figure 5.3.10. UC₂ densification on tungsten with square root of time.

Figure 5.3.11. UC_2 densification on niobium with square root of time.

Figure 5.3.12. UC_2 densification on tantalum with square root of time.

straight line. The R^2 value given represents the closeness of the fit: the closer to 1.0, the better the fit. Since the R^2 value for the tungsten data is >0.9 the straight-line fit is good. This supports the hypothesis that this zone sintering phenomenon is diffusion controlled. There is more spread in the data from the tests run at 2273 K, which may be attributed to difficulties experienced controlling the furnace during these runs. It was discovered later that the furnace heating elements had periodically shorted out and may have affected temperature control during some of these heats.

Since at time equal to 0.0 the densified height is also equal to 0.0, these equations should go through 0.0 if they are exact. There are two possible reasons as to why they do not go through 0.0: (1) a thin layer of WC is formed as the first carbon reaches the tungsten tray and with its lower diffusion coefficient delays the initial movement of carbon into the W, and (2) the timer in the furnace controller may be off enough to make this apparent delay in densification. It would only have to be off 8 to 10 seconds. The deviation from 0.0 is not great enough to warrant further testing.

The test results reported in this section show that when UC_2 (batch 5 composition) are sintered on Nb, Ta, or tungsten trays directional zone sintering will occur. The growth of the densified zone with time follows a parabolic relationship that indicates that directional zone sintering is diffusion controlled. Test results reported in Sections 5.5, 5.7, and 5.11 further address the issue of what is the primary diffusing species that affects this phenomenon.

5.4 Tests Studying the Effect of Temperature on UC_2 Densification

To observe the effect of temperature on sintering of UC_2 , a series of tests was done with UC_2 sintered on W, Nb, and tantalum for the same time (6 hours) at different temperatures. To assure consistency between heating tests, fresh pellets were pressed and new pieces of each metal were used for each heat. Table 5.4.1 contains the data from these tests, and Figure 5.4.1 is a simple plot of the height of the densified region vs temperature. The rate of growth increased dramatically with temperature. A second-order polynomial appears to fit each data set best.

Figure 5.4.1. Height of densified region vs temperature. Second order polynomial fit to each data set is shown.

Table 5.4.1. Densified Height on Tungsten, Niobium, and Tantalum, with Temperature

Temperature	W	Densified Height On Nb	Ta
(K)	(cm)	(cm)	(cm)
2023	0	0	0
2073	0.0762	0.0762	0
2123	0.0762	0.0762	0
2173	0.1524	0.1524	0.0762
2223	0.2540	0.2786	0.1270
2273	0.2540	0.3175	0.2159
2373	0.4826	0.5080	0.4445

Tantalum metal appears to be the least effective at initiating zone sintering. This may be because of its relative reactivity with carbon and the subsequent rate of diffusion of carbon into tantalum and tantalum carbide.

With this dramatic dependence on temperature, it may be that the rate of directional zone sintering follows an Arrhenius relationship. To consider this, include the relationship of the densified height vs $\sqrt{t}$ coupled with the Arrhenius diffusion equation revealed in Section 5.3.

First, a general solution of the equations describing diffusion of a single diffusing species moving into an infinite bar from one end is $x \approx 4 \sqrt{D \sqrt{t}}$, where x is distance into bar, D is the diffusion coefficient of the diffusing species, and t is the time. Applying this as analogous to the movement of the densified height through a UC_2 pellet, the equation can be rewritten as $h \approx 4 \sqrt{D \sqrt{t}}$, where h is the height of the densified zone and D is diffusion coefficient for the densified zone front.

Solving for D :

$$D \approx h^2/16t \quad ;$$

substituting $D^2/16t$ into the basic Arrhenius diffusion equation:

$$D = D_0 e^{-Q/RT},$$

where D_0 is the diffusion constant, Q is the activation energy, R is the gas constant, and T is the temperature (K), the following equation results:

$$h^2/t = 16 D_0 e^{-Q/RT}$$

If temperature dependence follows the Arrhenius relationship, a plot of $\log(h^2/t)$ vs $1/T$ should be a straight line. Such a plot of the data from Tables 5.4.1 and 5.3.2 is found in Figure 5.4.2. Note that a straight line can be drawn through each data set. The equations provide a reasonable fit to the data.

The slope of each line is equal to $-Q/R$ for each metal substrate used. From this relationship, an activation energy for directional zone sintering on each metal is determined. The results are shown in Table 5.4.2. It appears from the calculated Q values that the substrate metal may be a limiter on the rate of directional zone sintering. tungsten and Nb affect the rate of directional zone sintering almost identically, so either metal can be used to zone sinter UC_2 compacts with similar results.

Table 5.4.2. Directional Zone Sintering Activation Energy (Q) for UC_2 on Nb, Ta, and W Trays. Calculated From Empirical Data, Figure 5.4.2.

<u>Metal Tray</u>	<u>Slope</u>	<u>Q, Kcal/mole</u>
W	-6.5182	-129.5
Nb	-6.8832	-136.8
Ta	-9.1259	-181.3

5.5 Variable C/U Composition and Time Tests

Several test results in this work have shown that carbon diffusion appears to affect UC_2 densification. Since the diffusion coefficient for carbon in uranium carbide varies dramatically with composition (Figure 3.5.2), a test was run to see if other compositions exhibited the same directional zone sintering behavior and if the compositions with the highest diffusion coefficient values had the most rapid densification rate.

Figure 5.4.2. Effect of temperature on densification rate.

UC_x pellets from each composition were pressed and sintered at 2373 K in an argon atmosphere for the times indicated in Table 5.5.1. No problems occurred with any of the C/U level pellets on tungsten metal. On graphite, however the only pellet that did not stick was the one with a C/U level of 2.01. In every case the density increased with increased time. The highest density achieved was 97.8% TD at a starting composition of 1.88. Batch 5, with a starting C/U level of 1.95 reached a density of 96.4% TD. Only two starting compositions exhibited directional zone sintering, C/U = 1.95 and 2.01. The height of the densified region for the 1.95 C/U level pellets was over twice the height of that in the 2.01 level pellets.

It is evident from the results shown in Table 5.5.1 that directional zone sintering is not enhanced by carbon compositions with higher diffusion coefficients. In fact, only compositions with a carbon-to-uranium ratio of 1.95 or above exhibit the phenomenon.

Further characterization of the carbon level in pellets that exhibit zone sintering was desired. In order to observe the carbon weight per cent level along the axial direction perpendicular to the pellet/metal tray interface, a technique was developed to cut a pellet into thin slices and analyze for carbon. See Section 3.4.6 for description of the technique.

Pellets from batch 5 were mounted and sliced for carbon determination to observe the effects of composition, sintering time, and densification on carbon composition. Figure 5.5.1 contains a schematic of a typical sliced pellet showing the thickness and carbon level in each slice. Pellets from batch 5 were sintered at 2373 K on tungsten for 0.5 h, 3 h, 6 h, and 12 h. A pellet sintered for each time was sliced for carbon determination. Figure 5.5.2 shows a plot of the carbon data from each pellet. An approximate curve fit was drawn through each pellet's data set to observe how the relative carbon level changes with time.

Note that at the pellet/tungsten tray interface, (distance = 0.0), the weight per cent carbon is approximately 8.35 wt% after 0.5 h, but as the time at temperature increases, the interface carbon level decreases to somewhere below 8.15 wt% and stays at that level. In reality, as soon as carbon leaves the surface of the UC₂ pellet, the composition at the surface will drop to an equilibrium composition that depends on the activity of carbon in the two contacting substrates. The interface equilibrium carbon level between the UC₂ pellet at the batch 5 composition and tungsten metal substrate is estimated to be 8.10 wt% (C/U = 1.75), and the carbon concentration at the pellet surface is 0.076 mole/cc. If there is intimate contact between the pellet and tungsten substrate, the carbon activity should be the same in the W, and the concentration of C will be dependent on this activity level in both materials. If W₂C is formed, the carbon concentration would be

Table 5.5.1. Results of Variable C/U and Time Tests

C/U	Tray Material	Time (h)	Density (%TD)	Comments ^a
1.05	W	0.16	89.4	
1.05	W	0.5	91.1	
1.05	W	1	91.6	
1.05	W	3	92.7	
1.05	W	12	94.7	
1.30	W	0.5	83.8	
1.30	W	1	86.1	
1.30	W	3	89.6	
1.30	W	12	91.8	
1.30	Graphite	12	b	
1.50	W	0.5	89.4	
1.50	W	1	90.8	
1.50	W	3	92.5	
1.50	W	12	94.1	
1.50	Graphite	12	b	
1.88	W	0.5	93.5	
1.88	W	1	96.3	
1.88	W	3	96.5	
1.88	W	12	97.8	
1.88	Graphite	12	b	
1.95	W	0.5		h = 0.216 cm ^c
1.95	W	1		h = 0.500 cm
1.95	W	3	94.3	
1.95	W	12	96.4	
1.95	Graphite	12	b	
2.01	W	0.5		h = 0.089 cm
2.01	W	1		h = 0.229 cm
2.01	W	3		h = 0.330 cm
2.01	W	12	93.8	
2.01	Graphite	12	73.7	

^a Zone sintering occurred only where height of densification is shown.

^b Pellet stuck to tray.

^c h is the height of the densified region.

Figure 5.5.1. Example schematic of a sliced UC₂ pellet showing slice thickness and weight per cent carbon in each slice.

0.045 mole/cc, and if WC is formed, the carbon concentration would be 0.80 mole/cc. A test on carbon pickup in tungsten is presented in Section 5.7.

The carbon concentration drops dramatically up to 6 h at temperature, then the change is not nearly as rapid, although it does continue to drop. In order to see a possible connection between the carbon diffusing out and the densified region moving up the pellet, lines that show approximately where the top of each densified region is located (h) are included in Figure 5.5.2. It is evident from the length of each densified region that the top of each is below the position where carbon began to diffuse out, so it is not the diffusion front that triggers the densification.

It is also evident that the carbon concentration at the top of the densified zone is close to the same value of 8.55 wt% (within measurement error for h and weight percent carbon) for each sintering time, so the carbon level may be the most important parameter.

To look at batches with higher carbon than batch 5 to see if the same basic pattern holds when directional zone sintering occurs, pellets from batches 6 and 7 were prepared and sintered at 2373 K. First, a pellet from batch 6 that had been sintered at 2373 K for 6 h was mounted and sliced for carbon level determination (see Figure 5.5.3). The weight per cent carbon follows a pattern similar to that of batch 5 pellets, except that the shape of the carbon level curve is much steeper and the pellet/metal interface composition was higher at 8.25 wt%. The position of the top of the densified region intersects with the carbon weight per cent near 8.55 wt% as seen with batch 5.

Since this behavior held true for batch 6, which had a starting carbon level of 9.21 wt%, a test was done with batch 7, which had an even higher carbon level of 9.46 wt%, to see if it behaved in the same way. Pellets were pressed from batch 7 and sintered for various times at 2373 K. After sintering runs of 3, 6, and 12 h on a tungsten substrate, pellets at all three sintering times exhibited directional zone sintering. A pellet from each sintering time was mounted and sliced to measure the carbon level along the length of the pellet.

The carbon data for each pellet is plotted in Figure 5.5.4. Again, note how steep the carbon concentration curve is along the densified region of the pellets and that the height of this region correlates with the 8.55 wt% carbon level. It is interesting to see that the carbon concentration appears to level off near 8.50 wt% over the entire length of the densified region (see the 12-h pellet, Figure 5.5.4). The gradual concentration gradient followed by the steep concentration gradient along the length of the pellet indicates two different diffusion mechanisms may be involved between these carbon concentration levels. One thing is clear, though, when the carbon level is reduced to approximately

Figure 5.5.2. Weight per cent carbon from slices cut along axis of batch 5 UC_2 pellets sintered at 2373 K for various times.

Figure 5.5.3. Weight per cent carbon from slices cut along axis of a batch-6 UC_2 pellet sintered at 2373 K for 6 h.

Figure 5.5.4. Weight per cent carbon slices cut along axis of batch-7 UC_2 pellets sintered at 2373 K for 3, 6, and 12 h.

8.55 wt%, rapid densification begins. Further discussion of this conclusion is found in Section 6.0

No directional zone sintering occurred in the pellets made with batches 1, 2, or 3. It was observed that no discoloration due to carbon pickup occurred in the metals under these pellets. Evidently, the C/U compositions of 1.05 to 1.50 with phases of UC and U_2C_3 do not give up carbon to the substrate metal as do the higher compositions, so no active chemical gradient is created.

5.6 Tests on Molybdenum, Rhenium, and WC

Most of the sintering tests done in support of this investigation were done with UC_2 in contact with either tungsten, niobium, or graphite. Additional tests were done to observe the effect of using molybdenum (a carbide former), rhenium, and WC. UC_2 pellets were sintered on these trays for 3 hours at 2373 K in an argon gas atmosphere. The UC_2 pellet sintered on molybdenum melted onto the molybdenum piece, likely because of the low melting eutectic formed with uranium and molybdenum metals (see Figure 5.6.1). The UC_2 pellet sintered on rhenium slumped as if it were beginning to melt, again possibly due to a low melting eutectic formed between rhenium and uranium metals (see Figure 5.6.2). The UC_2 pellets sintered on WC did not react with the WC, nor did they exhibit any zone sintering, and the density achieved was much lower than pellets sintered on tungsten, niobium, and tantalum. Tungsten carbide seemed to be inert with UC_2 at high temperature, so it was used to test effects of other variables without interfering itself. This is because WC is a stable stoichiometric carbide that does not readily accept in-diffusion of free carbon, so no chemical gradient is created between UC_2 and WC. The carbon concentration in moles/cc is nearly identical between WC and UC_2 .

5.7 Tests on Carbon Pickup in Tungsten tray

Several observations were made of discoloration of the refractory metal pieces at the contact interface where the UC_2 pellets sat during sintering. Confirmation that this was formation of metal carbides and the rate at which it was occurring was desired, so UC_2

Figure 5.6.1. Mo-U phase diagram (Garg and Ackermann 1977).

Figure 5.6.2. Re-U phase diagram (Garg and Ackermann 1977).

pellets (batch 5, Table 3.5.1) were placed on tungsten and sintered at 2373 K for 4, 8, 12, and 16 hours. The tungsten pieces were cut through the position where each pellet sat, and were polished, etched, and examined for penetration depth of the carbon phase, see Figure 5.7.1. A hardness check was made on the metal and second phases. The hardness measured in the tungsten metal phase, ~500 dph, matched reported values. The hardness of the second phase measured ~1900 dph, which corresponds to tungsten carbide, but of which phase is not clear from the literature (Kieffer and Kolb 1949, Dolloff and Sara 1961). Storms (1990) indicated that under the conditions of these tests, the W_2C phase will form. Figures 5.7.2 and 5.7.3 show the polished cross sections of the tungsten/tungsten carbide pieces. It was difficult to measure the depth because it varied along the contact interface with the UC_2 , but it is evident that the depth continues to increase with time. Also, it is evident that carbide formation was more rapid directly under the edges of the pellets; contact must be better there than elsewhere.

Each of the four UC_2 pellets completely densified during this test. The density increased from 96.2% TD after 4 hours to 97.8% TD after 16 hours.

With the W_2C formation depth for different times, the diffusion coefficient D for carbon into W_2C can be estimated. Since the contact interface between the UC_2 and tungsten was not continuous, the maximum values were used as the best approximation, see Table 5.7.1.

Table 5.7.1. W_2C Formation Depth in Tungsten with Time

Time	Maximum Depth
<u>(sec)</u>	<u>(cm)</u>
14400	0.0432
28800	0.0772
43200	0.1057
57600	0.1219

W_2C

W

Figure 5.7.1. Tungsten carbide forming in a plate of tungsten metal. UC_2 pellet was located on top of tungsten carbide during sintering. Hardness indentations made with Vickers hardness tester (50x).

Figure 5.7.2. Tungsten carbide forming in tungsten metal after (a) 4 h and (b) 8 h (12.5x).

Figure 5.7.3. Tungsten carbide forming in tungsten metal after (a) 12 h and (b) 16 h (12.5x).

To estimate D , first plot depth vs $\sqrt{t}$, determine slope of the penetration data points, and use this relationship: $S(\text{slope}) \cong 4 \sqrt{D}$. Figure 5.7.4 shows a plot of these data. The data points fall in a straight line, so the equation fit is good. With a slope of 6.667×10^{-4} , D_{W_2C} is equal to $2.79 \times 10^{-8} \text{ cm}^2/\text{sec}$. This value is about 1/25 of the reputed literature value of $6.98 \times 10^{-7} \text{ cm}^2/\text{sec}$. In part this difference is because the literature values are based on diffusion of carbon in W_2C and the value determined empirically in this experiment is based on diffusion through a W_2C layer and formation of new W_2C at the W/W_2C interface. The W_2C penetration is really the reaction layer penetration and not a typical atomic diffusion penetration. Nevertheless, the value of D_{W_2C} determined in this way can help predict the rate carbon diffuses out of UC_2 pellets while being sintered in contact with tungsten metal.

5.8 Tests of Sintering Atmosphere

The standard atmosphere successfully used for most of the UC_2 sintering tests reported in this work was flowing argon gas. Tests were run to look at the effect of vacuum and the addition of hydrogen gas during the sintering cycle. The vacuum tests were done with pellets having different C/U ratios. One pellet from each composition was placed on W and one pellet of each was placed on graphite to be able to distinguish between general densification enhancement and directional zone sintering enhancement. The pellets were heated to 2373 K for 30 minutes in vacuum. Of the pellets sintered on W, only batches 5 and 6 with starting C/U of 1.88 and 1.95, respectively, exhibited zone sintering from the pellet-W interface, see Table 5.8.1. Because of zone sintering, the density was not determined for these pellets. The height of the densified zone in the batch 5 pellet sintered on tungsten was twice the height seen in tests done previously in argon atmosphere (see Figure 5.3.1), but the shrinkage was much less. The other pellets sintered uniformly. The pellets from batches 4 and 6 that were sintered on graphite were not as dense and did not exhibit directional zone sintering from the pellet-graphite interface. The batch 5 pellet that was sintered on graphite exhibited zone sintering from the end not in contact with the tray; the carbon ratio was 1.87 for the end in contact with graphite, and the other end was 1.85. This is thought to happen because at the high vapor pressure of carbon over UC_2 at this temperature (Storms 1967) in vacuum, carbon

Figure 5.7.4. Penetration depth of W_2C formed while sintering UC_2 on tungsten.

Table 5.8.1. Density Results of UC_x Pellets Sintered in Vacuum at 2373 K

Batch No.	x Value ^a C/U	Tray Material	Density (%TD)	Comments
2	1.30	W Graphite	85.8	Pellet broke apart.
3	1.50	W Graphite	90.8 90.9	
4	1.88	W Graphite	92.0 90.6	
5	1.95	W Graphite		Top and bottom ^b h = 0.343 cm from top ^b
6	2.01	W Graphite	58.7	h = 0.114 cm from bottom ^b

^a Value for starting powder.

^b Zone sintering.

diffused out of the exposed end of the pellet at a rapid rate. The outward diffusion of carbon from the exposed end of the pellet set up a diffusion gradient which apparently initiated the zone sintering phenomenon.

Lindemer (1972) reported that the presence of hydrogen gas increases the mobility of carbon atoms during the reduction of uranium dioxide with carbon and nitrogen carbide materials. It was hoped that the presence of hydrogen gas during the sintering cycle would also enhance densification in UC₂. To see if this would increase the zone sintering densification of UC₂, unfired UC₂ pellets (batch 5, Table 3.5.1) were placed on each of three metals, tungsten, niobium, and tantalum, and heated to 2123 K for 6 hours. At 1373 K, during the heatup cycle, a gas mix of 94% Ar + 6% H₂ was introduced into the furnace. This gas mix continued to flow through the furnace during the soak at 2123 K and until the furnace cooled to 1373 K, when the hydrogen gas was removed by evacuating and back filling with 100% argon gas. After the sintering heat, the pellets were measured to determine density. The pellets sintered slightly, but no zone sintering occurred, see Table 5.8.2.

Table 5.8.2. Results of UC₂ Sintering Tests in Hydrogen

Metal	Temperature	Zone Sintering/h (cm) ^a	Estimated ^b	Diameter ^c
	H ₂ Introduced (K)		Density (%TD)	Top/Bottom (cm)
W	1373	No	89	0.561
	2123	Yes/0.229	76	0.605/0.587
Nb	1373	No	89	0.561
	2123	Yes/0.178	76	0.605/0.587
Ta	1373	No	88	0.564
	2123	Yes/<0.030	--	N/A

^a h is the height of the densified region.

^b Estimated based on sintered diameters.

^c Starting Diameter = 0.648 cm.

NOTE: In argon atmosphere at 2123 K, the height of the densified region was 0.076 cm on W, and the sintered diameters were 0.589 cm on the low-density end and 0.550 cm on the high-density end.

The second test consisted of heating three fresh UC₂ pellets (batch 5) on the same metals, but this time the 94% Ar + 6% H₂ gas mix was introduced at the sintering temperature of 2123 K and was kept flowing until the end of soak, when argon was introduced before cooling down the furnace. This time each pellet began zone sintering from the end in contact with the metal. The height of the shiny densified region of pellets sintered on niobium and tungsten was twice that seen at the same temperature and time without the hydrogen addition, see Table 5.3.1. However, the amount of densification (diameter shrinkage) was much less than seen with UC₂ pellets sintered in argon gas at the same temperature. Again, the amount of zone sintering was much less on tantalum than the other two metals. Sintering UC₂ in a vacuum or partial H₂ atmosphere appears to enhance the rate the densified zone grows, but the density achieved is lower. Further tests are required before the effect of these atmospheres is fully understood.

5.9 General Behavior Tests

Early in this study, tests were done to look at the mobility of the high density/low density interface and to see whether once initiated, it would continue without the refractory metal contact. In one test, two green UC_2 pellets (batch 5) were stacked on top of each other and set on a piece of niobium metal. After 6 hours at 2373 K, the high density region had grown completely through the bottom pellet and one third up the length of the upper pellet, see the schematic in Figure 5.9.1.

In a second test, batch-5 UC_2 pellets were sintered on tantalum at 2373 K for 3 hours, and the high density region reached about one-third of the pellet length. The pellets were then placed on graphite, one with the high-density end in contact with the graphite and the other with the low-density end in contact with the graphite and reheated for 2 hours at 2373 K. Neither pellet sintered any further.

In a third test, two batch-5 UC_2 pellets were placed on niobium metal and sintered for 12 hours at 2373 K and both fully densified. The two pellets were then loaded into the furnace, one on graphite and other on niobium. A fresh UC_2 pellet was then placed on top of each sintered UC_2 pellet, and they were heated to 2373 K for 6 hours, after which no densification of the top pellets occurred. After 12 hours, the top pellets began sintering uniformly, but there was no evidence of zone sintering.

The results of the first test showed that the diffusing species that was shown in Sections 5.5 and 5.7 to be carbon moves readily across the interface between two pellets, and the densified zone front moves in the opposite direction across the pellet interface. The second test simply confirms that continual contact with the tantalum substrate was necessary to continue zone sintering. The third test also showed that metal contact is necessary for directional zone sintering, because as shown in Section 5.5, the carbon must reduce below approximately 8.55 wt% before the zone sintering can occur.

5.9.1. Schematic of high density regions of stacked UC_2 pellets on niobium after 6 hours at 2373 K.

5.10 Observations of Oxygen and Nitrogen Impurity Effects:

Occasionally during the course of this study, UC_2 pellets from batch 5 would sinter uniformly instead of from the end in contact with metal or they would exhibit a mild version of zone sintering, where the shiny end would develop, but the shrinkage was much less and the difference in diameter between high and low density ends was much less. Some of the pellets exhibiting this behavior were analyzed for oxygen and nitrogen and found to have oxygen up to 5000 ppm and nitrogen to 2000 ppm. This is much higher than the batch-5 pellets exhibiting typical zone sintering, see Table 3.5.1, so maybe these contaminants were influencing sintering behavior and affecting zone sintering.

A test run was made wherein UC_2 pellets were exposed to a glovebox atmosphere with 5 to 10 ppm oxygen for several days in an attempt to pick up oxygen. Oxygen pickup cannot be accurately verified in the green pellet state because, in addition to residual oxygen in the UC_2 , the binder and lubricant additives contribute several hundred parts per million. However, to estimate oxygen pickup in a green pellet exposed to the glovebox atmosphere, a UC_2 powder sample and a green pellet that had been exposed for 10 days were analyzed for oxygen. The oxygen level in the powder was 1900 ppm and in the pellet was 2480 ppm; therefore, the approximate amount of oxygen picked up was 580 ppm.

The pellets were heated for 10, 20, and 30 minutes in an argon atmosphere at 2373 K on tungsten metal. After the 10-minute sintering heat, the pellets exhibited zone sintering from the end in contact with tungsten. The height of the densified region was about 0.15 cm, but the diameter shrinkage was much less than seen in previous tests with batch 5. After 20 minutes, the zone sintering effect had disappeared, although there was still a small difference in diameter (0.015 cm) between the upper and lower ends of the pellet. After 30 minutes, there was no difference in diameter between the top and bottom end of the pellet. The density (estimated from diameter) was about 90% TD, which is higher than seen in batch 5 without zone sintering. After the 30-minute run, pellets were submitted for oxygen and the level had reduced to under 300 ppm. Unexpectedly, the nitrogen level had increased from the presintering level of 230 ppm to > 3000 ppm after sintering. Evidently nitrogen gas had entered the argon gas stream during the sintering cycle and reacted with UC_2 . It appears from this information that oxygen and nitrogen impurities may enhance overall densification, but they negate directional zone sintering.

The low density end of batch 5 pellets sintered for 30 minutes was typically 70 to 75% TD, compared to overall density of 90% TD achieved with high oxygen or nitrogen.

5.11 Duplex Pellet Tests:

Since directional zone sintering and densification has only occurred with UC_2 pellets in contact with carbide forming refractory metals, a test was designed to see if the refractory metal was a direct contributor to the process or simply acting as a carbon sink. To accomplish this, pellets were pressed with uranium carbide powders having two carbon concentration levels. One half of each pellet was pressed from powder from batch 5 having 8.96 wt% carbon, the optimum carbon level for zone sintering, and the other half of the pellet was pressed with powder from batch 3 having 7.04 wt% carbon. The pellets were placed on WC, which had been shown previously to be inert during UC_2 sintering and was not expected to initiate zone sintering (Section 5.6), and heated in an argon atmosphere to 2373 K for 30 minutes. One pellet was placed with the low carbon end in contact with the WC and the other vice versa. Another test was done exactly the same way except that the time was increased to 3 hours in hopes of completing the densification. If the carbon concentration gradient is the primary driving force for rapid zone sintering and densification, then densification should begin at the interface between the two compositions and proceed in the direction of the high C/U material.

As expected, the zone sintering began at the interface between the two compositions and proceeded toward the high C/U end. Figure 5.11.1 contains a photo of the duplex pellets after each sintering test. Note the much higher shrinkage in the high C/U end of the pellets. After 3 hours the pellets were completely densified. The interdiffusion of material at the interface between the two compositions was so complete that only the diameter change distinguishes between the two. One of the duplex pellets that had been sintered for 0.5 h was cut lengthwise, mounted, and polished to observe under a microscope the microstructure around the composition and density transition regions, see Figure 5.11.2. The materials at the composition interface had interdiffused and sintered to high density. The zone sintering front had moved about half way from the composition interface toward the end where $C/U = 1.95$. Note the dramatic difference in porosity across the zone sintering front. This provides conclusive evidence that the primary initiator of zone sintering in UC_2 is related to the diffusion of carbon. The

Figure 5.11.1 Sintered duplex composition UC_x pellets. C/U for one end, 1.95, and for the other, 1.50.

Figure 5.11.2. Photo of a partially sintered duplex composition pellet cut lengthwise and polished. Composition of high density end, $C/U = 1.5$, and low density end, $C/U = 1.95$.

refractory metals of tungsten, niobium, and tantalum do not aid the sintering, but simply provide the carbon concentration gradient and a sink for the diffusing carbon.

To further examine effects of carbon diffusion between the two compositions, duplex pellets that had been sintered for 0.5 hour, 3 hours, and 12 hours were sliced into thin wafers along the length and analyzed for carbon content. Figure 5.11.3 shows a plot of the results from these pellets. It is interesting to note how steep the carbon gradient still is between the two ends of the pellet after only 0.5 hour and how the slope begins to smooth out with increased time. As expected, carbon continues to diffuse down the concentration gradient, lowering the level in one end and raising it in the other end. Diffusion theory is supported by these data, which show that the carbon level at the interface between the two compositions rapidly reaches an equilibrium value and stays there with increased time. If the duplex pellets were heated long enough, the carbon level should be uniform from one end to the other.

To verify this behavior for UC_2 with an even higher carbon content, duplex pellets were made using batch 7 (9.46 wt% carbon) for one end and batch 3 (7.04 wt% carbon) for the other. The pellets were placed on WC and sintered for times of 0.5 h, 3 h, 6 h, and 12 h. Pellets from the three longer times were mounted, sliced, and analyzed for carbon content along the length. Figure 5.11.4 shows the carbon weight per cent values along the length of each pellet. As expected, the behavior was similar to that shown in Figure 5.11.3. The carbon content quickly diffuses toward the low carbon end. Figure 5.11.4 also shows the approximate length of the densified zone, which appeared in the batch 7 end of the pellet. As seen from the results described in Section 5.5, the top of the high density region corresponds to a carbon level near 8.55 wt%.

The results in this section provide conclusive evidence that the refractory metal substrates of niobium, tantalum, and tungsten were acting as carbon sinks and not contributing directly to the directional zone sintering phenomenon. Further evidence was also gathered from the duplex pellet carbon profiles that densification begins when the carbon level reduces below the 8.55 wt% level.

Further discussion of these results will follow in Section 6.

Figure 5.11.3. Duplex composition pellets weight per cent carbon profile after sintering at 2373 K.

Figure 5.11.4. Weight per cent carbon values along the length of UC_2 duplex pellets, carbon content 7.04 wt% on one end ($C/U = 1.50$) and 9.46 wt% on the other ($C/U = 2.07$), sintered for 3, 6, and 12 h on WC at 2373 K.

6.0 ANALYSIS AND DISCUSSION

The first objective of this investigation, to identify parameters important to the fabrication of high density UC_2 compacts by cold pressing and sintering at high temperatures, was met. Densities up to 97.7% TD were achieved with material having a carbon-to-uranium ratio of 1.88. High density was also achieved with higher carbon ratios if the compacts were sintered on refractory metal carbide trays. During the sintering run, however, the carbon-to-uranium ratio was reduced to below 1.86.

The key sample preparation parameters are given in Section 3. The key parameters for achieving high density include the following heating cycle in an argon atmosphere:

- 1 hour up to 723 K
- 1 hour hold at 723 K
- 1 hour up to 2373 K.

When pellet diameters exceeded approximately 0.74 cm, the heat-up time to 723 and 2373 K was increased to 2 hours for each step. After reaching 2373 K, the pellets are held for more than 6 h to complete densification. The furnace is cooled in 2 h to room temperature.

The trays used to achieve high density were made of niobium, tantalum, or tungsten metal. For UC_x where $x < 1.90$, WC proved successful and the carbides of niobium and tantalum will likely work also.

Using the parameters and processing techniques described in this investigation, fabricating UC_2 batches on a production basis should be possible. The only limitations would be the size of the synthesis and sintering furnaces and space in a high purity inert atmosphere glovebox system to process and store the UC_2 material.

If impurities of oxygen and/or nitrogen can be tolerated in the uranium dicarbide material, high density can be readily achieved in shorter times. The presence of these impurities seems to negate the zone sintering effect but enhances movement of material and subsequent densification.

A right cylindrical pellet with carbon level above 8.55 wt% was sintered on carbide-forming refractory metal, and the length-to-diameter ratio increased. In other words, the pellet shrank more in the diameter than in length. This probably has to do with preferential grain growth along certain crystallographic planes that are perpendicular to the carbon diffusion direction. If this can be verified with controlled sintering tests, it would be very important to controlling behavior of UC_2 pellets or compacts at high temperature.

Attempts to enhance densification and grain growth with the use of sintering aids were not successful. Niobium and tantalum were used because they were associated with the directional zone sintering phenomenon and nickel because it had been successfully used in uranium monocarbide. The higher melting refractory metals seemed to play no role at all in densification and did not inhibit directional zone sintering when present in the matrix. Each of these metals forms carbides with high melting points. A lower melting additive that is compatible with UC_2 is desired.

The second major objective, to experimentally investigate the mechanism for densification of UC_2 compacts on graphite, tungsten carbide, and refractory metal substrates, including tungsten, niobium, tantalum, rhenium, and molybdenum, was also successfully completed. A mechanism for densification of UC_2 compacts is proposed in this section.

Sintering UC_x pellets on refractory metals where the x is >1.88 revealed an interesting phenomenon. As shown in Section 5.1, densification of uranium dicarbide pellets where the x is >1.88 begins at the interface between the pellet and the metal substrate and proceeds up the length of the pellet. As shown in Figure 5.1.6, this behavior actually occurred from any contact interface with the refractory metal. Since the rate of growth of the high density region was shown to be proportional with the square root of time, it was postulated that this densification must be related to or dependent upon the diffusion of a single diffusing species. The diffusing species was shown experimentally to be carbon. To confirm this, tungsten that had been in contact with UC_2 during sintering picked up carbon, evidenced by formation of a W_2C layer and pellet slices analyzed for carbon revealed a carbon concentration gradient from the pellet metal interface to the other end of the pellet.

Typically, diffusion of atoms such as carbon across a chemical (concentration) gradient from one material to another follow the relationship shown in Figure 6.0.1. The difference in composition at the interface is due to the carbon activity in each material. Since the carbon activity has to be equal, the composition will vary from one material to another. In the case of tungsten, described in Section 5.7, the carbon does not diffuse into tungsten, but forms W_2C at the diffusion front, so the actual carbon profile looks like the dashed line shown in Figure 6.0.1. Figure 5.7.2 reveals the distinct demarcation between the W_2C phase and the tungsten metal phase.

Figure 6.0.1. Typical concentration profile for diffusion of material C across a chemical gradient between materials A and B .

The diffusion of carbon out of UC_2 for batch 5 followed the pattern shown for material *B* in Figure 6.0.1. Figure 5.5.2 indicates that after 0.5 h, the diffusion of carbon had not reached equilibrium with W_2C/W at the pellet metal interface but by 3 h, it had.

This is not true, because at the interface between UC_2 and tungsten, carbon will diffuse rapidly to equalize the carbon activity on both sides. If the sample for carbon were thin enough, it would have shown the 8.10 wt.% carbon level. The sample submitted was several millimeters thick and was therefore a bulk sample. Since carbon diffusion is directly related to the appearance of the direction zone sintering phenomenon, a model for the carbon concentration was desired. Using Figure 6.0.1 as a basic picture of what the carbon concentration should look like in UC_2 (material *B* side), an equation for $C(x,t)$ was desired. Referring to Figure 6.0.1, for materials *A* and *B*, C is the concentration, x is the position along the horizontal axis, and t is time.

For $t > 0$,

$$C_B(x,t) = a_1 + b_1 \operatorname{erf}(x/C_1 \sqrt{D\sqrt{t}}) \quad (1)$$

Two boundary conditions: (1) $C_B(\infty, t) = C_i$

$$(2) \quad C_B(0, t) = C'$$

$$C_A(x,t) = a_2 + b_2 \operatorname{erf}(x/C_2 \sqrt{D\sqrt{t}}) \quad (2)$$

Two boundary conditions: (1) $C_A(\infty, t) = 0$

$$(2) \quad C_A(0, t) = C'$$

Apply boundary conditions (1) and (2) to Eq. 1:

$$C_B(0, t) = C' = a_1 + b_1 0 \quad (\operatorname{erf}(0) = 0), \text{ therefore } a_1 = C'$$

$$C_B(\infty, t) = C_i = C' + b_1 \operatorname{erf}''(\infty), \text{ so } b_1 \text{ therefore } C_i - C'$$

Therefore:

$$C_B(x,t) = C' + (C_i - C') \operatorname{erf}(x/C_1 \sqrt{D\sqrt{t}}) \quad (3)$$

For C_A , apply boundary conditions:

$$(1) C_A(0,t) = C' = a_2 + b_2(0), \text{ therefore } a_2 = C'$$

$$(2) C_A(\infty,t) = 0 = C' + b_2(1), \text{ therefore } b_2 = -C'$$

Therefore:

$$C_A(x,t) = C' - C' \operatorname{erf}(x/C_2 \sqrt{D\sqrt{t}}) \quad (4)$$

Since the top of the densified zone is below the position where carbon begins to diffuse out (diffusion front) of the UC_2 pellet (see Figure 5.5.2), equation (3) does not describe directly the position of the densified height h . Since the densified height occurs at a position where the carbon composition was approximately 8.55 wt%, this can be used to calculate a position dependence with time. In order to do this, use the values for C_i and C' shown in Figure 5.5.2 and assume $C(x,t)$ is 8.55. Equation (3) becomes:

$$8.55 = 8.10 + (8.66 - 8.10) \operatorname{erf}(x/C_1 \sqrt{D\sqrt{t}}) .$$

$$\text{Let } C_1 = 4, \text{ so } \operatorname{erf}(x/4\sqrt{D\sqrt{t}}) = 0.80 .$$

From the error function table, if $\operatorname{erf}(\) = 0.80$, the quantity $(\) = 0.9139$; therefore,

$$\begin{aligned} 0.9139 &= x/4\sqrt{D\sqrt{t}} \text{ and} \\ x &= 3.6564\sqrt{D\sqrt{t}} . \end{aligned} \quad (5)$$

The Arrhenius equation presented in Section 5.4 should be modified to reflect this change as follows:

$$h^2/t = 13.36 D_0 e^{-Q/RT} \quad (6)$$

In order to match the values of x with the value of h measured in this investigation, the value of D was determined iteratively by varying D with t until x closely matched h for all values of t .

This was done with data from Table 5.3.2 for tungsten. First, the calculated values for position (x) were plotted directly with the plot of the height of the densified region, h , vs time, Figure 6.0.2. As seen from the plot, the values of $D = 8.047 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $D = 9.0 \times 10^{-7} \text{ cm}^2/\text{sec}$ closely match the measured values. To more closely pick the best matching value for D , the measured position values were plotted against the calculated values in Figure 6.0.3. From this plot, it is obvious that a D value of 8.047×10^{-7} provides the best fit to the measured values; in fact, nearly a perfect fit below 0.5 cm. Above 0.5 cm, the measured values are higher than the calculated values. This may be because carbon is diffusing out of the pellet from all surfaces during a sintering run and with increased time, the carbon level in the exposed end of the pellet approaches the critical level and densification begins rapidly. Also, the error function equation is based on the assumption that length of the pellet is several times greater than $\sqrt{Dt}$, so as the height of the densified region approaches the end of the pellet, diffusion is affected by the open end. Because D is determined in this way, it is termed the “effective” diffusion coefficient. It describes the movement of the high density zone through the length of a UC_2 pellet when sintered in contact with a refractory metal substrate. This value of D relates to the D value for carbon diffusion through equation (3).

The same approach was taken for UC_2 sintered on niobium and tantalum. Plots of calculated versus measured values for height of densified region appear in Figures 6.0.4 and 6.0.5. Note that the effective diffusion coefficient for carbon diffusing in UC_2 while sintering on niobium is also around $8.0 \times 10^{-7} \text{ cm}^2/\text{s}$ and above 0.5 cm, the densified region grows much faster than predicted by the carbon diffusion equation.

There appears to be more scatter in the calculated versus measured data when sintering on tantalum, but the best effective diffusion coefficient is around $5.5 \times 10^{-7} \text{ cm}^2/\text{s}$. Table 6.0.1 summarizes the diffusion coefficient data just presented for sintering of UC_2 on niobium, tantalum, and tungsten substrates at 2373 K.

Figure 6.0.2. Plot of the measured height h of densified region with time and calculated values at different D values. On tungsten.

Figure 6.0.3. Measured vs calculated position of densified height with various D values. On tungsten.

Figure 6.0.4. Measured vs calculated position of densified height with various D values. On niobium.

Figure 6.0.5. Measured vs calculated position of densified height with various D values. On tantalum.

Table 6.0.1. Effective Diffusion Coefficient for Carbon Diffusion in UC₂ and the Movement of Densified Region Through all UC₂ Pellets

<u>Metal Substrate</u>	<u>Effective D(cm²/s)</u>
Nb	8.047 x 10 ⁻⁷
Ta	5.5 x 10 ⁻⁷
W	8.047 x 10 ⁻⁷

Table 6.0.2. Estimated D₀ Values for UC₂ Sintering on Niobium, Tantalum, and Tungsten

<u>Metal Substrate</u>	<u>D₀(cm²/s)</u>	<u>D₀(cm²/s)</u>
	<u>From D(T) Effective</u>	<u>From Arrhenius Plot</u>
Nb	7.42 x 10 ⁵	4.05 x 10 ⁶
Ta	2.75 x 10 ¹⁰	3.63 x 10 ¹⁰
W	7.42 x 10 ⁵	7.31 x 10 ⁵

The values from both approaches agree reasonably well. These values should not be compared directly to D₀ for straight carbon diffusion in UC₂ because the process discussed here includes the variables of carbon diffusion, densification of UC₂, and formation of carbide in a refractory metal substrate. It is interesting to note, though, that effective D values shown in Table 6.0.1 compare very closely with the calculated literature values plotted in Figure 3.5.2.

To see how D determined from UC₂ pellets sintered on Nb, Ta, and tungsten compares to D calculated from duplex pellets, data from Figure 5.11.2 was used in Equation 3. D values were calculated over a range of ± 0.15 cm around the composition interface for the three different times. The calculated values varied from 1.0 x 10⁻⁷ cm²/s to 11.3 x 10⁻⁶ cm²/s, but the average was 5.5 x 10⁻⁷ cm²/s. This is identical to the value for UC₂ on tantalum, but a little lower than the values determined for sintering on niobium and tungsten. This was not pursued any further because:

- the length of each composition segment was too short for ideal diffusion equation;

- accurate determination of carbon values was hindered by oxygen pickup during sampling; and
- general loss of carbon occurred during sintering.

Another check was made of the diffusion coefficient using the data from a pellet sintered for 3 h on tungsten and sliced for carbon determination. Calculated values of $C(x,t)$ from Equation (3) were plotted with measured values from Figure 5.11.2 (3 h). Figure 6.0.6 shows this plot. Note that 0.1 wt% carbon was added to all values above 8.5 because they picked up 0.1 to 0.2 wt% oxygen during sampling. As a qualitative test, the value of $D = 8.0 \times 10^{-7} \text{ cm}^2/\text{s}$ provides a good match to the measured values.

One of the most important points of this analysis is not only to relate the growth of the densified region to carbon diffusion but to examine why UC_2 will not densify until the carbon composition reduces to below the 8.55 wt% level. To understand this, examine the phase diagram proposed by Storms, see Figure 6.0.7. Note that points 1, 2, 3, 4, 5, 6, and 7 are added onto the graph at 2100 C. These points represent the starting batch numbers from Table 3.5.1 and show the composition position in the phase diagram. Batches 1, 2, 3, and 4 sintered completely, and all are located in the $\text{UC} + \text{UC}_2$ two-compound region. Batches 5, 6, and 7 exhibited directional zone sintering and are all located in the two-phase $\text{UC}_2 + \text{free carbon}$ region. Herein lies the key; uranium dicarbide containing free carbon will not densify, apparently because the free carbon interferes with uranium and subsequent pore mobility in the crystal structure. The effective diffusion rate of the free carbon is low, though, so the concentration gradient created by outward diffusion is steep. Below the free-carbon level, carbon diffusion appears to be higher, so the carbon concentration gradient is much less steep. The results from batch 7 shown in Figure 5.11.4 support this hypothesis. Another factor affecting the diffusion of carbon from the free carbon region is the high porosity (nearly 35% even after 12 hours), which inhibits solid diffusion, so vapor diffusion may be the primary mechanism. In fact, as the high density front sweeps through the pellet, the primary means of transport across interface between the high and low density region and between the low and higher carbon concentration may be vapor species. It is not only the carbon that must move, but for pore sweeping and resultant densification, uranium atoms must also be moving. For complete understanding of this process, further analysis is needed.

Figure 6.0.6. Comparison of measured and calculated carbon level at various distances from the pellet end. Sintered for 3 h at 2373 K.

Figure 6.0.7. Phase diagram of the U-UC₂ system. (Storms 1967)

6.1 Future Work

The discovery of the directional zone sintering phenomenon and the associated diffusion mechanism warrants further study from both an academic viewpoint and one of practical interest. Compatibility concerns during high temperature operations are frequently related to the diffusion of atoms such as carbon from the base material to containment and structural components. The rate of this diffusion under various conditions is very important information. Understanding of the fundamental mechanisms, such as the rate of formation of carbides in refractory metal components and subsequent diffusion rate of carbon, is needed for predicting component lifetime.

Further study is warranted to more precisely determine activation energies and diffusion coefficients of carbon in UC_x when in contact with refractory metals so that uranium carbide components can be accurately fabricated with duplex density structures to enable control of internal porosity and carbon diffusion.

One of the basic mechanisms in directional zone sintering is not defined. Is the primary mechanism for uranium and carbon movement at the densification front vapor or solid transport or a combination of the two? Understanding this would help in prediction of behavior under high temperature conditions and would help with techniques to control microstructures.

7.0 CONCLUSIONS

1. UC_x high density compacts can be fabricated with a final $x = 1.88$ and a composition of 95 vol% tetragonal UC_x .
2. Densities greater than 97% TD and grain sizes up to $37\ \mu\text{m}$ are achievable with a cold press and sinter techniques.
3. UC_x will not densify on substrates that do not remove some of the carbon when $x > 1.88$.
4. There is an equilibrium composition for UC_x ($x \approx 1.88$) at which all free carbon atoms are bound in the uranium matrix. Densification starts almost instantaneously from the surface reaching this composition.
5. Propagation of the densification front is controlled by the rate of carbon diffusion from the uranium dicarbide samples to the substrate having a lower carbon activity. The carbon level profile can be predicted from this equation:

$$C(x/t) = C' + (C_i - C') \operatorname{erf}(x/4 \sqrt{D}\sqrt{t}).$$

6. The higher the carbon ratio, the longer the time before densification is initiated and the slower the densification front will move through a UC_x pellet.
7. The rate of movement of the densification front is predictable with diffusion equations:

$$h = 3.6564 \sqrt{D}\sqrt{t}$$

8. The activation energies, diffusion constant, and example diffusion coefficients can be determined with the data presented herein.

Table 7.0.1 Summary of Directional Zone Sintering of UC_2 on Refractory Metal Substrates: Activation Energies and Diffusion Constants

Metal Substrates	Q	D_0	D
	(kcal/mole)	cm^2/s	cm^2/s^a
Nb	-136.8	4.05×10^6	8.05×10^{-7}
Ta	-181.3	3.63×10^{10}	5.5×10^{-7}
W	-129.9	7.31×10^5	8.05×10^{-7}

^a Calculated based on 2373 K.

SELECTED BIBLIOGRAPHY

Ainsley, R., B. R. Harder, N. Hodge, R. G. Sowden, D. B. White, and D. C. Wood, "Carbides as Reactor Fuels: Preparation from Oxides and Sintering Characteristics," in *New Nuclear Materials Including Non-Metallics*, Proceedings of the Conference on New Nuclear Materials Technology, Including Non Metallic Fuel Elements, IAEA, Prague, July 1963 (IAEA, Vienna, 1963).

Alcock, C. B., H. A. Eick, E. G. Rauh, R. J. Thorn, "A Comparison of the Calculated and Observed Vaporization Behavior of the Uranium Dicarbide Phase," in *Nuclear Metallurgy, Vol X*, IMD Special Report No. 13, The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers.

Alexander, C. A., J. J. Ward, J. S. Ogden, and G. W. Cunningham, "Thermodynamics for Compatibility Studies of Metal Clad Uranium Carbide," in *Carbides in Nuclear Energy, Vol I: Physical and Chemical Properties, Phase Diagrams*, Edited by L. E. Russell, B. T. Bradbury, J. D. L. Harrison, H. J. Hedger, and P. G. Maardon (Macmillan and Co Ltd, London, 1964).

Anthonyamy, S., P. R. Vasudeva Rao, and C. K. Mathews, "Carbothermic Synthesis of Carbides of Uranium and Plutonium," Indira Ghandi Centre for Atomic Research report IGCAR-82 (1986).

Ashbee, K. H. G., F. C. Frank, and C. K. H. DuBose, "On the Bainitic Transformations in Uranium Carbides," *Journal of Nuclear Materials*, **47**(1973).

Austin, A. E. "Carbon Positions in Uranium Carbides," *Acta Cryst.* **12** 159 (1959).

Benz, Robert, and J. D. Farr, "X-Ray Diffraction of UC-UC₂ and UC-UN Alloys at Elevated Temperatures," *Journal of Nuclear Materials* **42** 217-222 (1972).

Borg, Richard J., and G. J. Dienes, *An Introduction to Solid State Diffusion*, (Academic Press, Inc., Harcourt Brace Jovanovich, San Diego, California, 1988).

Bowman, Allen L., G. P. Arnold, W. G. Witteman, T. C. Wallace, and N. G. Nereson, "The Crystal Structures of UC₂," *Acta Cryst.* **21** 670 (1966).

Brett, N., D. Law, and D. T. Livey, "Some Investigations on the Uranium:Thorium:Carbon System," *Journal of Inorganic Chemistry* **13** 44-53 (1960).

Catlow, C. R. A., "The Diffusion of Carbon and Oxygen in Uranium Dicarbide," *Journal of Nuclear Materials*, **60** 341-343 (1976).

Chang, Roger, "A Diffusionless UC₂ (Cubic) to UC₂ (Tetragonal) Transformation," *Acta Cryst.* **14** 1097 (1961).

DePoorter, Gerald L., and T. C. Wallace, *Diffusion in Binary Carbides*, (Academic Press, Inc., New York, 1971).

Dollaff, R. T., and R. V. Sara, Wright Air Development Division Report WADD-TR-60-143, Part II, Wright-Patterson Air Force Base, Ohio (1961).

- Ervin, Guy, Jr., "Uranium and Plutonium Carbides with Tungsten Additives," *Ceramic Bulletin*, **50** (8) 659-661 (1971).
- Frost, B. R. T., "The Carbides of Uranium," *Journal of Nuclear Materials* **10** (4) 165-300 (1963).
- Gillam, E., "A Geometrical Relationship Between UC_2 (Tetragonal) and U_2C_3 (Cubic)," *Acta Cryst.* **15** 1183 (1962).
- Gulden, T. D., "Carbon Thermal Diffusion in the UC_2 -C System," *Journal of the American Ceramic Society* **55** (1) 14-18 (1971).
- Gupta, S. K. and Gingerich, K. A. "Observation and Atomization Energies of the Gaseous Uranium Carbides, UC , UC_2 , UC_3 , UC_4 , UC_5 , and UC_6 by High Temperature Mass Spectrometry," *Journal of Physical Chemistry* **71** (7) 3072-3080 (1979).
- Imoto, S., T. Sano, and Y. Takada, "Studies on Uranium Dicarbide and Sesquicarbide," in *Carbides in Nuclear Energy, Vol 1*, Edited by L. E. Russell, B. T. Bradbury, J. D. L. Harrison, H. J. Hedger, and P. G. Mardon (Macmillan and Co Ltd, London, 1964).
- Kalish, H. S., U. S. Atomic Energy Commission report TID-7589 (1960).
- Kaufman, Larry and Ann Sarney, "Thermodynamic Properties of Transition Metal Monocarbides," in *Nuclear Metallurgy, Vol X*, IMD Special Report No. 13, The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers.
- Kieffer, R., and F. Kolbl, *Powder Metallurgical Bulletin* **4** 4 (1949).
- Kingery, W. D., H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd Edition, (John Wiley and Sons) 1976.
- Kurasawa, T, K. Shiozawa, S. Nasu, T. Kikuchi, and Y. Uchida, "Transmission Electron Microscopic Studies of Twin Structure of Uranium Dicarbide," *Journal of Nuclear Materials* **45** 63-66 (1972/73).
- Kurasawa, T, H. Watanabe, and T. Kikuchi, "Transformation to U_2C_3 Phase in UC - UC_2 and UC_2 Phases," *Journal of Nuclear Materials* **43** 192-204 (1972).
- Kofstad, Per, *High Temperature Corrosion* (Elsevier Applied Science, London and New York, 1988).
- Kuczynski, G. C., A. E. Miller, and Q. A. Sargent, Editors, *Sintering and Heterogeneous Catalysis* (Materials Science Research, 1984).
- Laugier, J. and P. L. Blum, "Le Diagram Metastable UC - UC_2 ," *Journal of Nuclear Materials* **39** 245-252 (1971).
- Leitnaker, J. M. and T. G. Godfrey, "Thermodynamic Properties of Uranium Carbides," *Journal of Nuclear Materials* **21** 1750180 (1967).

Lindemer, T. B., M. D. Alden, and J. J. Leitnaker, "Kinetics of the Graphite-Uranium Dioxide Reaction from 1400° to 1756°C," *Journal of the American Ceramic Society*, **52**(5) 233-237 (1969).

Lindemer, T. B. "Rate Controlling Factors in the Carbothermic Synthesis of Advanced Fuels," *Nuclear Applications and Technology* **9** 711-715 (1970).

Macleod, A. C., "High-Temperature Thermodynamic Properties of Uranium Dicarbide," *Journal of Inorganic Nuclear Chemistry*, **31** 715-725 (1969).

Matzke, HJ., and C. Politis, "Self-Diffusion of Uranium in Uranium Dicarbide UC₂," *Solid State Communications* **12** 401-404 (1973).

Matthews, R. Bruce, and Richard J. Herbst, "Uranium-Plutonium Carbide Fuel for Fast Breeder Reactors," *Nuclear Technology* **63** 9-22 (1983).

Oetting, F. L. and J. D. Navratil, "The Chemical Thermodynamic Properties of Nuclear Materials (II) High Temperature Enthalpy of the Uranium Carbides," *Journal of Nuclear Materials* **45** 271-283 (1972/73).

Ohse, R. W., J. F. Babelot, K. A. Long, and J. Magill, "Vapour Pressure Measurements of Uranium Carbides up to 7000 K using Laser Pulse Heating," in *Thermodynamics of Nuclear Materials, 1979, Vol 1*, Proceedings of an International Symposium on Thermodynamics of Nuclear Materials, IAEA, Julich, Germany, January-February, 1979. (IAEA, Vienna, 1980).

Resnick, R. R. Steinitz, and L. Seigle, "Determination of Diffusivity of Carbon in Tantalum and Columbium Carbides by Layer-Growth Measurements," in *Transactions of the Metallurgical society of AIME* **233** 1915 (1965).

Resnick, R., and L. Seigle, "The Diffusion of Carbon in Tantalum Monocarbide," *Transactions of the Metallurgical Society of AIME* **236** 1732-1738 (1966).

Routbort, J. L. and HJ. Matzke, "Grain-Boundary Diffusion of Uranium in Pure and Doped Uranium Carbides with Different C/U Ratios," *Journal of the American Ceramic Society* **58** (3-4) 81-84 (1975).

Sasaki, N., K. Kubo, and M. Asano, "Vaporization and Surface Ionization of LaC₂, CeC₂, PrC₂, NdC₂, ThC₂, and UC₂," *Journal of Nuclear Science and Technology* **8**(11) 614-421 (1971).

Sears, M. B., and L. M. Ferris, "Studies on the U-C Constitutional Diagram between UC and UC₂," *Journal of Nuclear Materials* **32** 101-112 (1969).

Stoops, R. F., and Hamme, J. R., North Carolina State College Report NSCS-2663-9, North Carolina State College, Raleigh, North Carolina, (1962).

Storms, E. K., *Refractory Materials, A Series of Monographs, Vol II*, (Academic Press, New York, 1967).

Suzuki, H. and S. Kimura, "On the Behavior Referred to the Transformation of UC_2 at High Temperatures," *Bulletin of the Tokyo Institute of Technology*, No. 69, 49-54 (1965).

Suzuki, Yasufumi, Kenichi Shiozawa, and Muneo Handa, "Solubility of Tungsten in Uranium Monocarbide," *Journal of Nuclear Science and Technology* **21**(8), 608-613 (1984).

Suzuki, Yasufumi, Yasuo Aria, Tatsuo Sasayama, and Hitoshi Watanabe, "Kinetics on Carbothermic Reduction of UO_2 + C Powder and Compacts of UC_2 ," *Journal of Nuclear Science and Technology*, **19** (3) 222-230 (1982).

Tagawa, Hiroaki, "The Variation of Lattice Parameter with Carbon Content of Non-Stoichiometric Uranium Dicarbide," *Journal of Nuclear Materials* **34** 116-118 (1970).

Tagawa, H., K. Fujii, Y. Sasaki, "Studies on the Uranium Dicarbide Phase," *Journal of Nuclear Science and Technology* **8**(5), 244-249 (1971).

Van Vlack, Lawrence H., *Elements of Materials Science*, 2nd Edition, (Addison Wesley Publishing Co., Inc.) 1964.

Wallace, T. C., W. C. Witteman, C. L. Radosevich, and M. G. Bowman, "Carbon Diffusion in the Carbides of Uranium," presented at the High Temperature Materials Sixth Meeting, 1968.

Wilson, W. B., "High Temperature X-Ray Diffraction Investigation of the Uranium-Carbon System," *Journal of the American Ceramic Society* **43**(2) 77-81 (1960).

Zope, B. D., and V. K. Moorthy, "Reaction Sintering of Uranium Monocarbide," in *Transactions of Indian Ceramic Society* **34**(3) 51-59(1975).

This report has been reproduced directly from the best available copy.

It is available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831. Prices are available from (615) 576-8401, FTS 626-8401.

It is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.