FOREWORD

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This report covers work for the 12-month period through April 30, 1961.

R. T. Dolloff has served as supervisor for the work reported and R. V. Sara has been the principal investigator. Contributions to the technical effort also were made by W. J. Kroenke, J. D. Ruggiero, C. E. Lowell, and F. J. Beodray. Acknowledgment is made for guidance and helpful suggestions to J. C. Bowman and N. R. Thielke.

ABSTRACT

The work here reported is the result of an investigation of phase equilibria in the binary system, tungsten-carbon. A tentative phase diagram is presented which differs significantly from the one proposed by Sykes in 1930 and which is generally accepted today. The data were obtained by high-temperature differential thermal analysis and classical quenching procedures, both supplemented by metallographic, X-ray, and chemical techniques.

Results for the tungsten-carbon binary system indicate a eutectic between W and W_2C at 2735°C, and a eutectic between W_5C_3 and C at 2765°C. The W_2C lattice accommodates 72 and 74 atomic per cent W at 2475° and 2735°C, respectively. Carbon solubility is evident only at 2540°C, the eutectoid temperature. A new phase, W_5C_3, has been discovered which is stable only above 2540°C. WC decomposes at 2730°C into W_5C_3 and C.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
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RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES

I. INTRODUCTION

A. Objective

Space age requirements for high-temperature materials have created considerable interest in metal-carbon systems primarily because of their high melting temperatures and hardness. To fulfill these requirements, precise information relative to phase equilibrium relations at high temperatures is imperative. In addition to information regarding the melting temperatures of selected compositions, phase studies provide data necessary for the achievement of compositions free of subsolidus transformations such as phase changes or precipitations which may have deleterious effects in high-temperature structural elements.

The work reported here has, therefore, been directed to the determination of accurate phase equilibrium relations of selected metal-carbon systems at high temperatures. Considerable effort has been applied to extension of reliable experimental techniques to the necessary high temperatures and to the attainment of high quality results.

B. The Tungsten-Carbon System

Selection of the tungsten-carbon system as the object of this program has been based on the importance of tungsten and carbon as super-refractory elements. Equally as significant in this capacity are the compounds of W_2C and WC. Furthermore, these compounds represent some of the hardest man-made materials. Retention of this property at high temperatures has led to widespread use in tool and structural applications. The investigation of phase relations in the tungsten-carbon system has presented an opportunity to apply and improve techniques, particularly those of high-temperature differential thermal analysis, for measurements at temperature higher than those encountered in the Si-B-C system previously reported. The research was undertaken in the belief that these precision techniques would materially aid in clarifying errors in the previously accepted tungsten-carbon phase diagram. The present report validates this hypothesis.

C. Review of Literature

The phase equilibrium diagram of the tungsten-carbon binary system shown in Figure 1 is essentially that presented by Schwartzkopf and Kieffer[1] and by Hansen,[2] and as suggested by Norton.[3] By means of X-ray diffraction studies, Norton determined the homogeneity range of W_2C as depicted on the diagram except for carbon solubility at 2525°C which he found to be negligible. The remaining features are the

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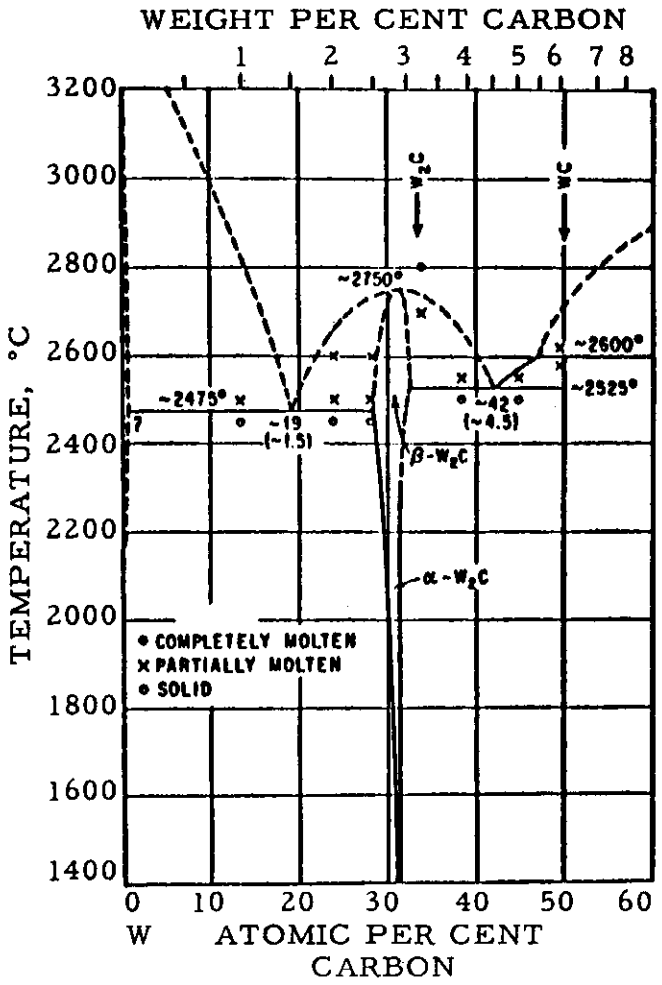

Figure 1. - W-C Phase Diagram According to Sykes

same as those published by Sykes.[4] Schwartzkopf and Kieffer,[1] in their survey of the tungsten-carbon system, concluded that the system detailed in Figure 1 may be regarded as fairly reliably established.

The existence of two stable carbide phases, W_2C and WC, was originally established by Andrews[5] in 1923, and by Becker[6, 7, 8] in 1928. Prior to these efforts, all other investigators worked with alloys of tungsten and carbon produced by melting a mixture of the elements under a carbon arc or in a carbon crucible. This procedure yields melts with carbon content which varies from surface to center unless the melt has been saturated with carbon at temperature. A combination of chemical and microstructural analysis, on samples with such widely varying composition, has been, at best, an uncertain method of identifying the existing phases.

By studying the reaction between incandescent tungsten and naphthalene vapor, Andrews[5] was able to show the existence of W_2C and WC. The presence of both compounds was identified by the appearance of inflections on the resistance-composition curve.

Becker,[6,7,8] in a study of the carbon-tungsten system, heated tungsten filaments in an atmosphere of benzene and hydrogen in which the partial pressure of carbon and the temperature of the filament were controlled. From X-ray diffraction patterns of selected carbonized filaments, he was able to identify WC, W_2C, and an additional phase which he characterized by X-ray diffraction and other physical measurements as a high temperature modification of W_2C.

Sykes,[4] in a classical paper, proposed a phase diagram of the tungsten-carbon system based on metallographic and X-ray considerations. His results are shown in Figure 1, along with a few representative points.

Many different melting temperatures have been reported for W_2C and WC.[1] In the most recent investigation, Nadler and Kempter[9] report a eutectic temperature between W and W_2C of 2733°C, and a melting temperature of 2720°C for WC. Nadler and Kempter gave careful consideration to temperature measurement methods and materials in the course of obtaining these data and similar type information on other carbides and eutectics.

II. PROCEDURES AND EQUIPMENT

A. Sample Preparation

1. Raw Materials

The raw materials employed in these studies consisted of tungsten powder obtained from the General Electric Company, tungsten-carbide powder obtained from the Firth Sterling Company, and Acheson graphite powder obtained from the National Carbon Company. The chemical analyses of the three raw materials are listed below:

TABLE 1

CHEMICAL ANALYSIS OF RAW MATERIALS

W	WC	C
99.14% W 0.05% C 0.90% O	93.72% W 6.15% C 0.11% O	>99.99% C

2. Hot- and Cold-Pressing

Hot- and cold-pressing techniques were used to prepare homogeneous samples containing from 10 to 90 atomic per cent carbon. Tungsten, graphite, and tungsten-carbide (WC) powders were thoroughly blended by tumbling overnight to

provide the desired composition. Hot-pressing was carried out at 1800°C in carbon molds, fitted with carbon pistons, placed into a four-inch diameter carbon tube furnace containing an argon atmosphere. Pressures employed ranged between 4000 psi and 6000 psi. The cylindrical specimens removed were 3/8-inch in diameter and approximately one-inch in length. They showed less than 0.5 atomic per cent change in composition during hot-pressing.

Pellets measuring 3/16-inch in diameter and of similar length were fabricated by cold-pressing at a pressure of approximately 40,000 psi without benefit of binders. The samples normally were presintered in vacuo at around 1100°C to ultimately permit drilling of a 0.040-inch hole along the sample axis. This practice simplified sample suspension in the furnace for differential thermal analysis and quench studies.

B. Differential Thermal Analysis (DTA)

1. Weight-Gain Studies

To evaluate the feasibility of pursuing phase studies on tungsten-carbon compositions in a carbonaceous environment, a series of weight-gain studies was made on hot-pressed samples to determine the extent of carbon absorption under conditions identical with the proposed differential thermal analysis study. This was felt necessary because the entire DTA apparatus is constructed of carbon or graphite.

In all weight-gain experiments, the specimens were contained in graphite DTA sample holders and heat-treated in a carbon resistance furnace. In constructing the weight-gain curves, it was assumed that weight-gain resulted from carbon pick-up. This was verified by chemical analysis of test specimens at the conclusion of these experiments. Thorough considerations of time and temperature dependence were given to compositions representative of the $W-W_2C$ and W_2C-WC phase areas. It was generally observed that reaction of the samples was appreciable if free tungsten was present. Figure 2 shows the compositional change of two samples representative of the W-WC and $WC-WC_2$ phase areas. The samples were heated five minutes at each of the temperatures represented by a datum point. It is apparent from this figure that reaction with carbon of specimens containing free tungsten was appreciable even at 2200°C. On the basis of these data and photomicrographs, it is evident that DTA in carbonaceous environments is of limited value in analyzing samples containing less than 33 atomic per cent carbon.

2. DTA with Graphite: Boronated-Graphite Elements

The differential thermal analysis apparatus developed in these Laboratories has been successfully used to temperatures of 3000°C, and has played a major role in the evaluation of phase relations in the Si-B-C system.[10] A differential thermal analysis unit of the type successfully used in the study of Si-B-C alloys and in the present study is shown in Figure 3. The sensitivity of this device is somewhat greater than that for Chromel-Alumel over virtually the entire temperature range from 25 to 3000°C. Hot-pressed pellets of the type previously described are contained in one of the two graphite capsules which are shown bridged by the short, boronated graphite rod. This assembly is heated in a tubular graphite resistance

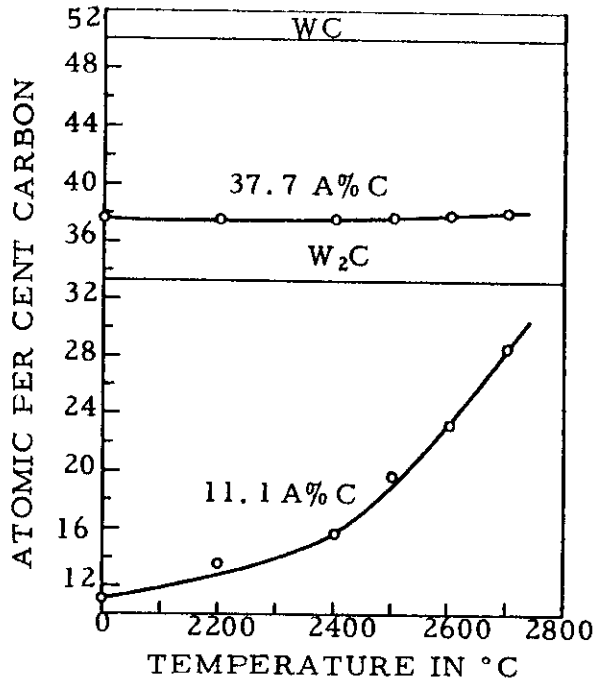

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Figure 2. - Temperature Dependence of Composition for Samples Containing 11.1 and 37.7 Atomic Per Cent Carbon

R3-1296

Figure 3. - Differential Thermal Analysis Unit

furnace under an atmosphere of argon. Thermal analysis in this study was limited to compositions containing more than 33 atomic per cent carbon to avoid side reactions with the carbonaceous environment, as discussed previously. Typical thermal data obtained for compositions representative of the phase areas W_2C-WC, WC-C, and WC are shown in Figure 4. These thermal effects, averaged from several runs, may be summarized as follows:

TABLE 2

AVERAGED THERMAL EFFECTS OBSERVED IN COMPOSITIONS BETWEEN W_2C AND C

	Heating	Cooling
W_2C-WC	2525°; 2770°	2760°; 2525°
WC, WC-C	2730°; 2765°	2770°; 2525°

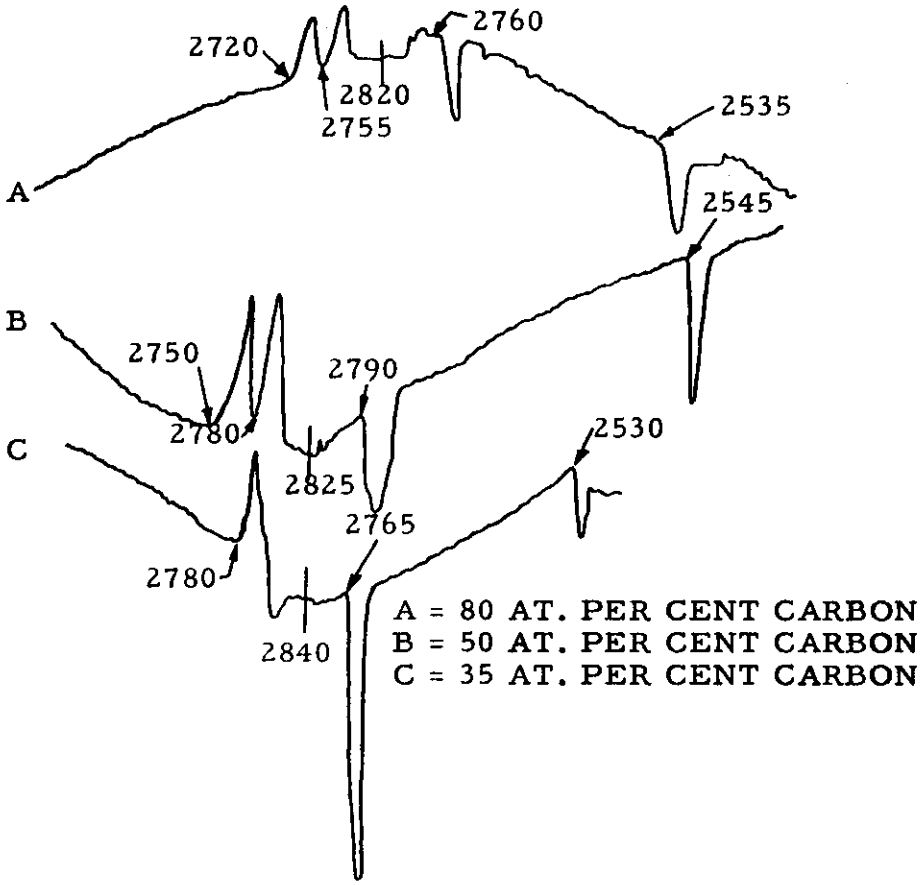


Figure 4. - Differential Thermal Analysis Data Representative of the Areas WC-C, W_2C-WC, and WC

In the phase area W_2C-WC, endothermic heat effects, which are reversible on cooling, are noted at 2525°C and 2770° on heating. For WC, and in the phase area WC-C, a double heat effect, which is irreversible under these experimental conditions, is observed around 2750°C. Fusion was observed to take place in samples containing between 35 and 50 atomic per cent carbon.

3. DTA with Tungsten-Rhenium and Tantalum-Rhenium Elements

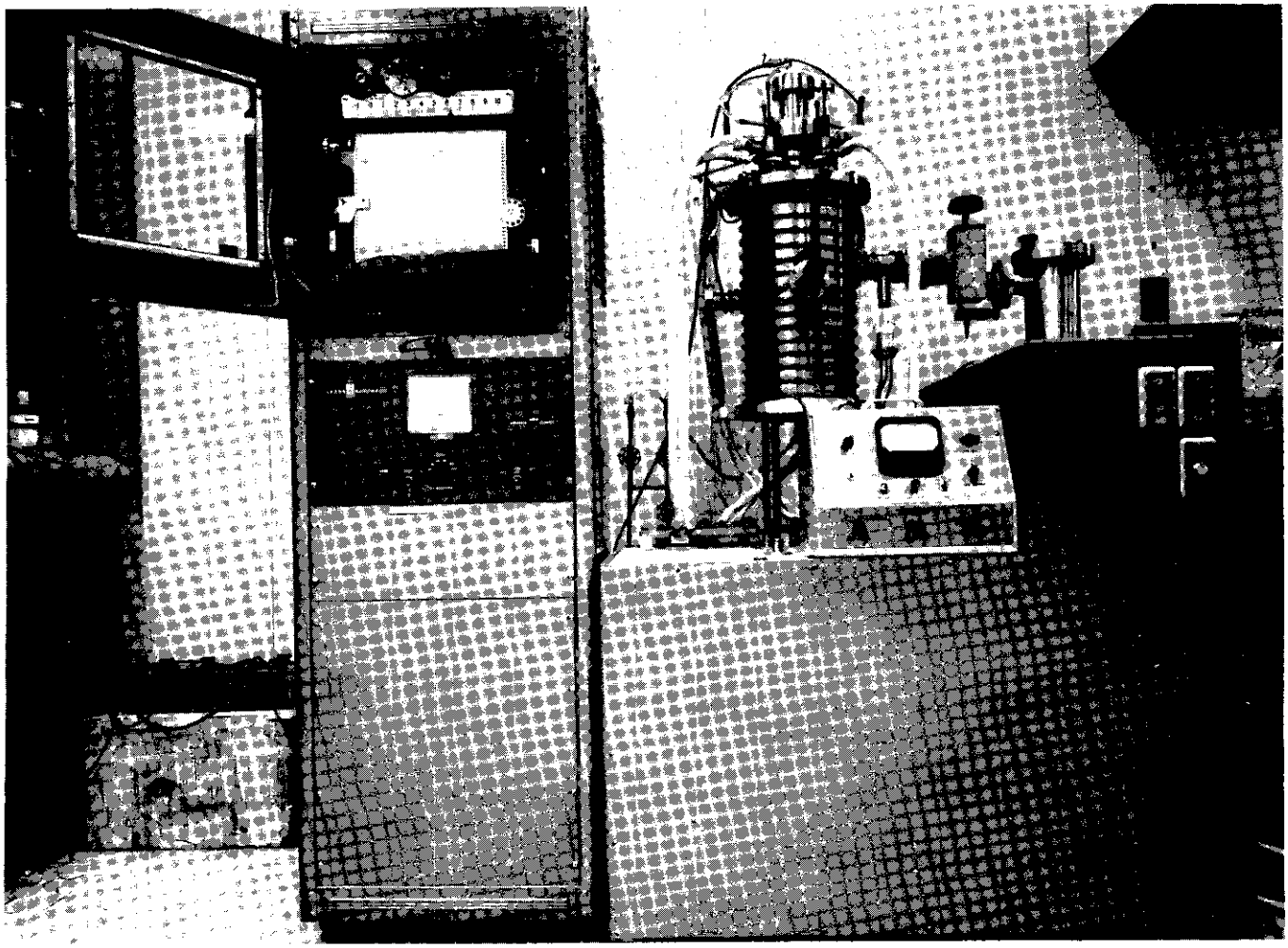
Differential thermal analysis studies conducted with graphite-based thermocouples have been very useful in analyzing that portion of the phase diagram between ditungsten carbide and carbon. However, because of the reactive nature of high tungsten alloys with carbon, this procedure is not directly applicable for all temperatures and compositions. An attempt, therefore, was made to exploit the method of differential thermal analysis with the aid of thermocouples of tungsten-rhenium and of tantalum-rhenium. Preliminary efforts with W-Re elements provided measurable signals in the course of melting platinum, but no heat effects were observed in alloys with compositions between W and W_2C for temperatures up to 2600°C. These results may not be conclusive because the sensitivity of these elements decreases substantially at temperatures above 2200°C. The same type behavior was noted also with the tantalum-rhenium elements. Because of the negative character of these results, consideration is currently being given to a thermocouple based on W and an alloy of W-Re which reportedly[11] has a better sensitivity to 2800°C than the other metallic couples mentioned above.

C. Quench Studies

1. Furnace Equipment

To expedite analysis of phase relationships in that portion of the system containing less than 50 atomic per cent carbon, the classical procedure of quenching was adopted. A vacuum furnace of the type shown in Figure 5 was designed and constructed for these experiments. The vessel measured 10 inches in diameter and 20 inches in height. The unit, which is water-cooled, and all related accessories are of stainless steel. A resistance-heated container for molten tin can be incorporated on the bottom for the purpose of quenching samples. The samples can be dropped into the molten tin at any time by means of a fuse wire arrangement installed on the furnace head. Three sight ports at 90° to each other are located midway on the furnace and provide means for temperature measurements on various faces of the sample.

The heating element used for these studies consisted of a tantalum tube, 10 inches long, one-inch in diameter, and with a wall thickness of 0.015-0.020 inch. The furnace is capable, however, of being heated by a variety of tubular elements either under conditions of vacuum or inert gases at one atmosphere pressure.



N-966

Figure 5. - Furnace Equipment

2. Temperature Measurements

A disappearing filament-type optical pyrometer, manufactured by Leeds and Northrup Company, was used for temperature measurements. The pyrometer was calibrated through a window of the type contained on the furnace against a National Bureau of Standards calibrated tungsten ribbon lamp. Temperatures referred to in this report pertain to that of the sample surface which was found to closely approximate black body conditions. This was verified by comparing the temperature of the interior of a small hole drilled in a sample with the temperature of the adjacent surface. At 2500°C, the surface appeared to be approximately 20° higher. The accuracy of temperatures reported, therefore, is believed to be approximately ±20°C.

3. Thermal Treatment of Specimens

Compositions considered for the quenching experiments were varied between W and WC in such quantities as to delineate phase areas within one atomic per cent. Pellets prepared by cold-pressing were suspended in the furnace by a 0.005-inch diameter tantalum wire drawn through an axial hole. The samples in all cases were first heated in vacuo to 1500°C to expel all gases. The furnace was then purged twice with pure argon at room temperature, and all high-temperature runs were then carried out under approximately one atmosphere of argon. Prior to use of these procedures, it had been observed that samples were stripped of carbon under a vacuum of 10^{-5} mm of Hg and temperatures of 2500°C. Under conditions of argon atmosphere, the samples appeared homogeneous and exhibited negligible structural or compositional gradients as a result of decarburization.

A total of approximately 65 samples was quenched from high temperatures. Generally, samples were held at temperature for one hour up to 2600°C, and for progressively shorter times as the temperatures were increased. In most instances, quenching was accomplished by quickly shutting off the heater power. As a typical example of the quenching rate, samples cooled from 2600°C to 1500°C in 20 seconds and to 1000°C in an additional 40 seconds. Samples with compositions between W_2C and WC were quenched by dropping into molten tin held at a temperature of 250° to 300°C.

D. Analytical Techniques

Phase analyses of quenched samples were accomplished primarily by metallographic and X-ray techniques. In all cases, a direct correlation was found between visual and X-ray analysis methods. Hardness measurements aided in establishing the number and character of existing phases in microstructures. Microhardness values of 470, 1450, and 2085 kg/mm^2 were established as being representative of W, W_2C, and WC, respectively. It was not possible to establish solid solution ranges by lattice parameter measurements because precipitation occurred in all cases.

III. THE TUNGSTEN-CARBON SYSTEM

A. Experimental Procedures

1. The W-W_2C Eutectic

The eutectic temperature between W and W_2C was determined to be 2735°C. This temperature was obtained by visually observing specimens as they were heated slowly through the temperature region and noting first signs of melting. Specimens held for longer periods of time, at 10 to 15° below this temperature, were studied metallographically to validate the absence of a liquid phase. Melting was observed in samples containing 10, 20, and 25 atomic per cent carbon. Nadler and Kempter[9] recently reported a eutectic temperature of 2733°C, which agrees with these observations. Photomicrographs, Figures 6 and 7, reveal the structural change accompanying melting for a composition containing 25 atomic per cent carbon. The light areas seen in Figure 6 are W_2C; the dark areas are W. In Figure 7, the dark areas are a eutectic phase.

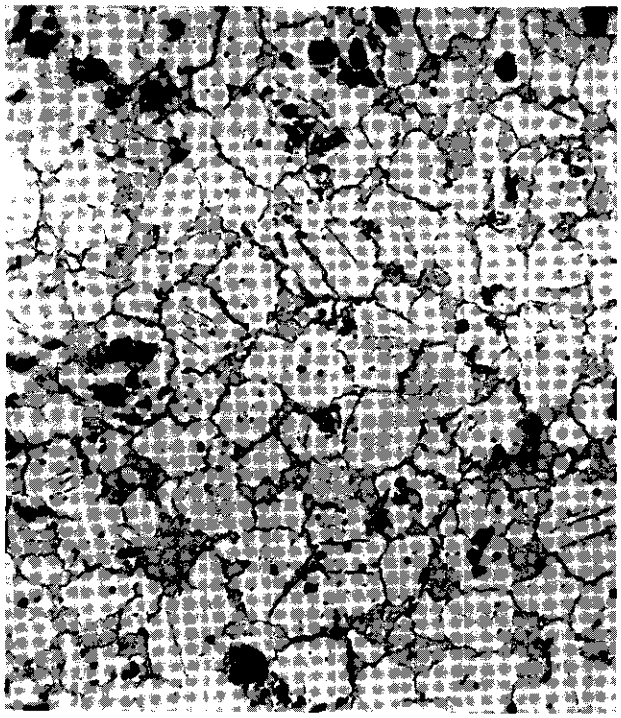


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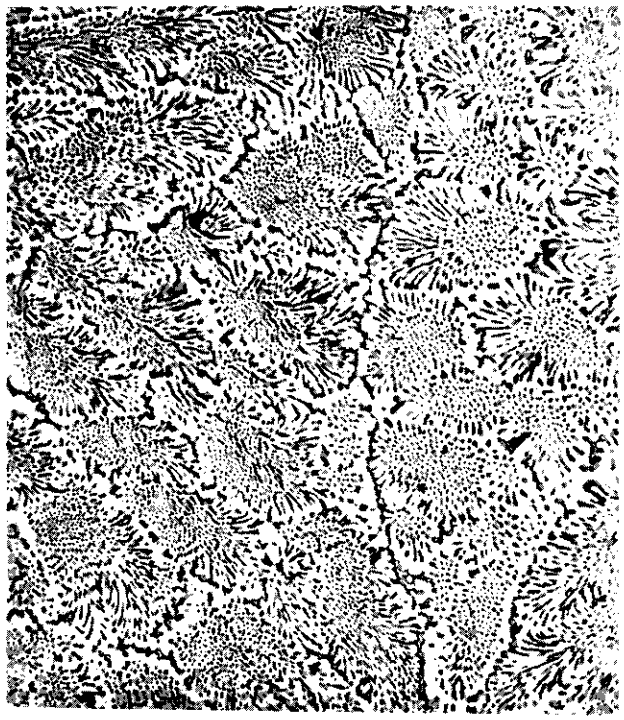
Figure 6. - Microstructure of Samples Containing 25 Atomic Per Cent Carbon at 2725°C - 240X Magnification



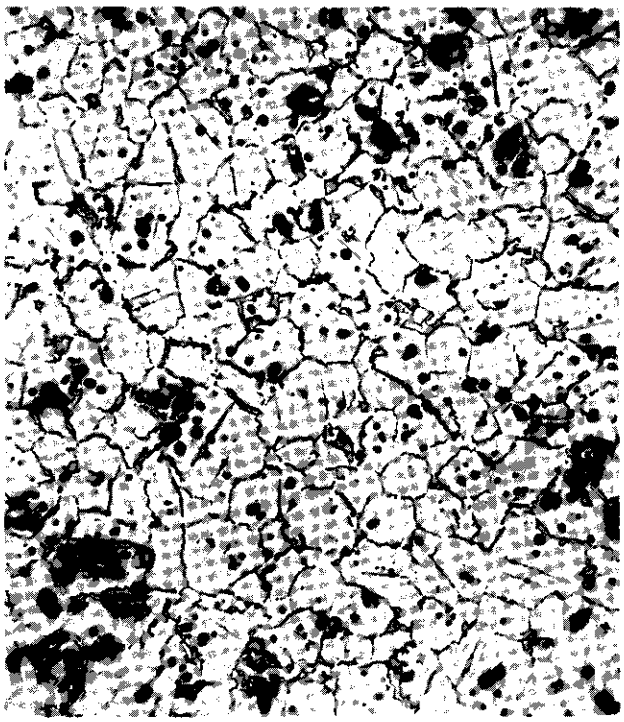
N-1265

Figure 7. - Microstructure of Samples Containing 25 Atomic Per Cent Carbon at 2750°C - 240X Magnification

No attempt has been made to establish the extent of carbon solubility in tungsten, the eutectic composition, or the liquidus.

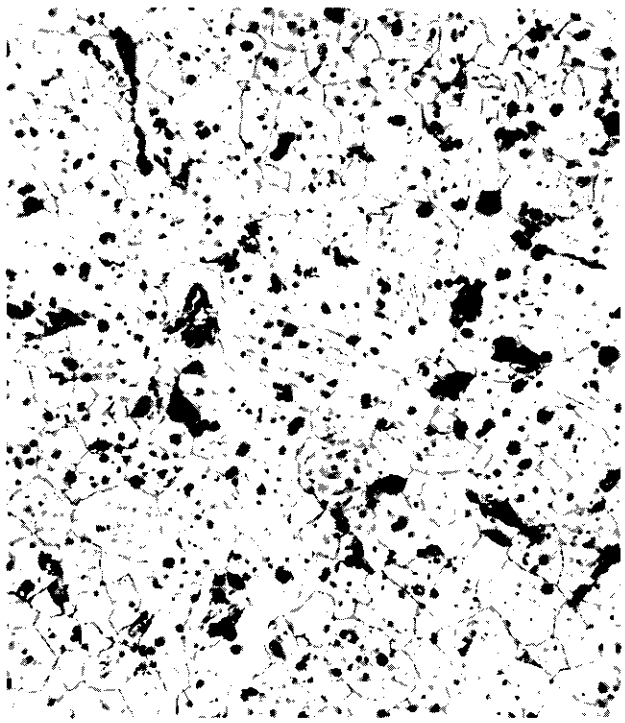
2. Homogeneity Limits of W_2C

The limits of W solubility in W_2C were determined at 2475°C and near the eutectic temperature (2735°C). This was accomplished by quenching samples whose compositions were varied by 1-2 atomic per cent carbon and observing the absence of grain boundary tungsten in photomicrographs. At 2475°C, the limit of solubility of tungsten in W_2C corresponded to a composition containing 72 atomic per cent tungsten. This limiting composition also could be noted as $W_{2.57}C$. Figures 8 and 9 show microstructures of compositions which bracket $W_{2.57}C$ by one atomic per cent carbon. Figure 8 shows the presence of tungsten in the grain boundaries as a discrete phase and not as a precipitate.



N-1267

Figure 8. - Microstructure of Samples Containing 27 Atomic Per Cent Carbon at 2475°C - 240X Magnification

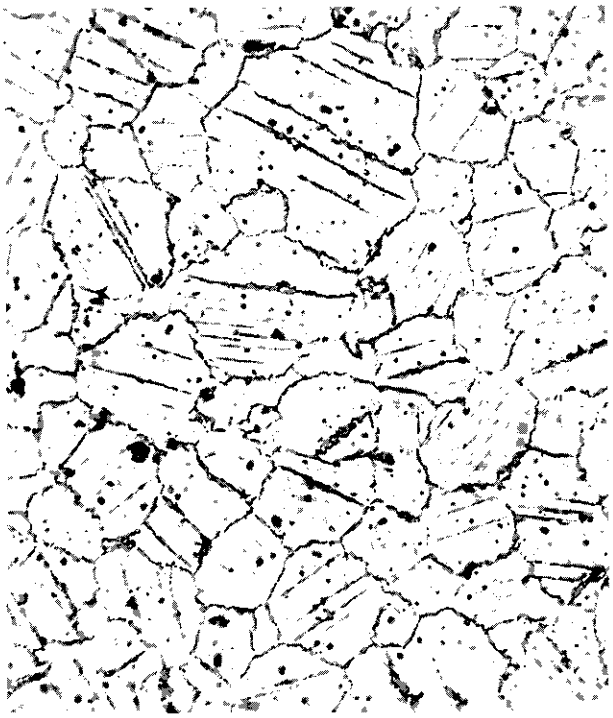


N-1266

Figure 9. - Microstructure of Samples Containing 29 Atomic Per Cent Carbon at 2475°C - 240X Magnification

Tungsten solubility in W_2C increases only slightly at higher temperatures. The limiting composition near 2735°C corresponds to 74 atomic per cent tungsten, or the formulation $W_{2.84}C$. Figure 10 (27 atomic per cent carbon) shows the absence of grain boundary tungsten, whereas in Figure 6, this phase is readily apparent.

On the carbon-rich side at 2475°C and 2700°C, the limiting composition was established as $W_{2.00}C$. Near the eutectoid temperature of 2540°C, W_2C can take carbon into solution. Evidence of this behavior can be seen in Figure 11. The composition is based on 35 atomic per cent carbon and from all appearances is single phase. A WC precipitate is apparent in the photograph as the familiar lamallae.



N-1268

Figure 10. - Microstructure of Samples Containing 27 Atomic Per Cent Carbon at 2760°C - 240X Magnification

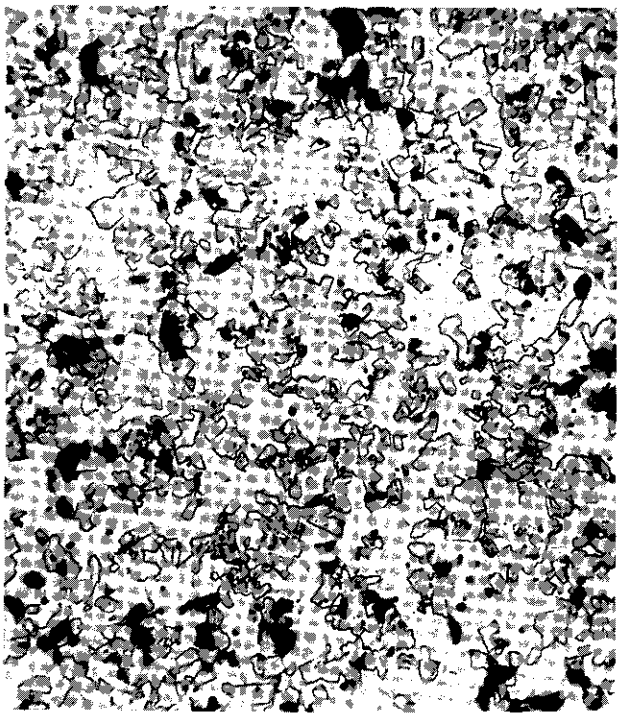
N-1269

Figure 11. - Microstructure of Samples Containing 35 Atomic Per Cent Carbon at 2550°C - 240X Magnification

Stoichiometric W_2C was heated to 2775°C without melting, whereas Sykes[4] reports congruent melting at 2750° ±50°C. Further attempts will be made to melt this material when conversion is made to a tungsten heater element and higher temperatures can be attained.

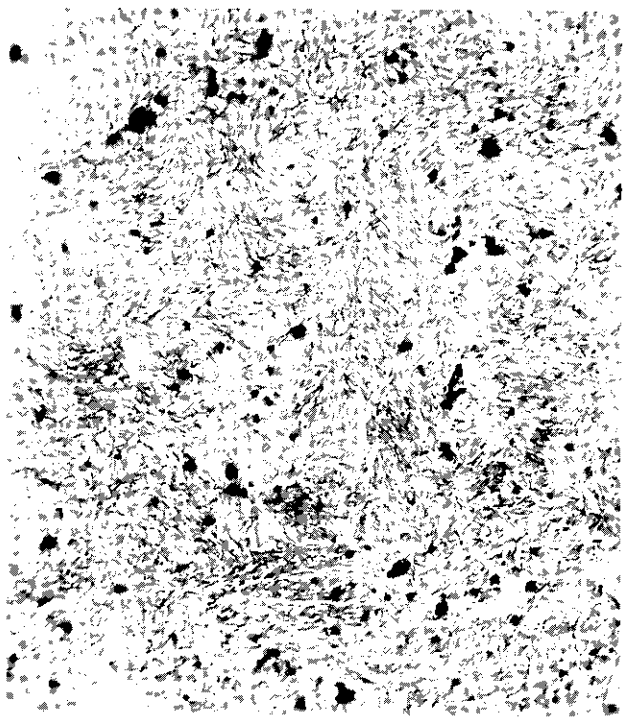
3. The W_2C-WC Eutectoid

The eutectoid temperature between W_2C and WC was determined as 2540°C by quenching a number of samples from above and below this transformation temperature. The microstructural change associated with this reaction is shown in Figures 12 and 13. Figure 12 pertains to a specimen containing 40 atomic per cent carbon heated to 2520°C just below the eutectoid reaction temperature. The microstructure indicates a two phase aggregate of W_2C and WC, with WC representing the darker of the two components. Figure 13 refers to a similar specimen heated slightly above the eutectoid. The new phase, which formed above 2540°C, decomposed on cooling to provide the microstructure depicted in this figure. The photomicrograph represents a decomposed product of W_2C and WC. The samples described above were obtained by the simple cooling method of quickly shutting the heater power off. The cooling rate obviously was not fast enough to freeze in the high temperature phase. The eutectoid reaction temperature of 2540°C determined from these experiments, however, correlates remarkably well with a heat effect at 2525°C observed in the differential thermal analysis studies.



N-1270

Figure 12. - Microstructure of Samples Containing 40 Atomic Per Cent Carbon at 2520°C - 240X Magnification



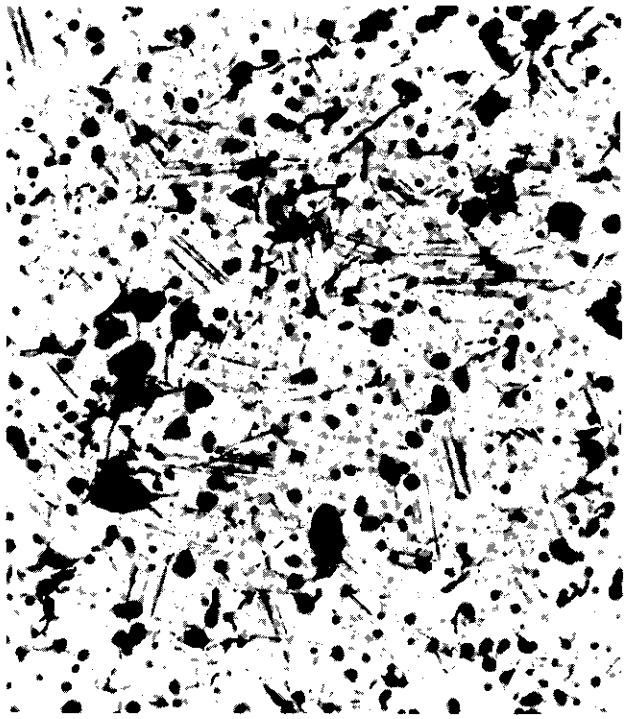
N-1271

Figure 13. - Microstructure of Samples Containing 40 Atomic Per Cent Carbon at 2550°C - 240X Magnification

To delineate the high-temperature area containing γ, a new phase, a faster quenching rate into molten tin was employed. It was not possible to suppress decomposition even by this rapid quenching process, but it was considerably easier to detect secondary phases in microstructures, a task which had proved to be difficult in the more slowly cooled specimens. In specimens tin-quenched from 2600° and 2700°C (Figures 14 and 15), all γ was observed only in compositions containing 37 and 38 atomic per cent carbon. The specimen containing 37 atomic per cent carbon (Figure 14) has tabular-like grains which attain this appearance

N-1442

Figure 14. - Microstructure of Samples Containing 37 Atomic Per Cent Carbon at 2700°C - 240X Magnification



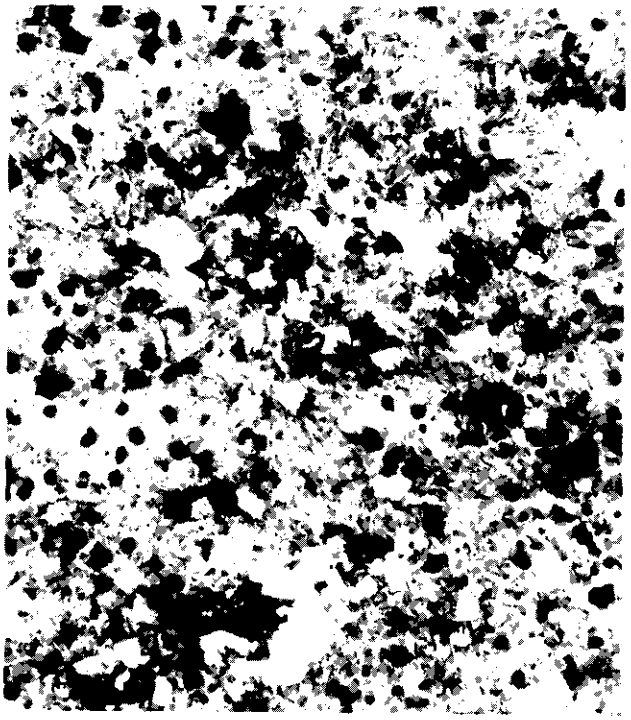
N-1443

Figure 15. - Microstructure of Samples Containing 38 Atomic Per Cent Carbon at 2700°C - 240X Magnification

from the lamallae of precipitated W_2C. The specimen corresponding to 38 atomic per cent carbon shows this to a lesser extent. Microstructures for specimens of 36 and 39 atomic per cent carbon, Figures 16 and 17, show secondary phases of W_2C and WC, respectively. In view of the narrow homogeneity limits established for the γ phase and its proximity to 37.5 atomic per cent carbon, it appears justifiable to assign a formulation of W_5C_3 to this high-temperature phase.

N-1444

Figure 16. - Microstructure of Samples Containing 36 Atomic Per Cent Carbon at 2700°C - 240X Magnification



N-1445

Figure 17. - Microstructure of Samples Containing 39 Atomic Per Cent Carbon at 2700°C - 240X Magnification

The implications of the foregoing comments (Subsection 3) are summarized in Figure 18 as a partial phase diagram. The number associated with each datum point refers to the respective photomicrograph. These photomicrographs represent only 12 of approximately 65 which were examined. They are of major importance, however, for they serve to define to within one atomic per cent, the major phase areas in the system.

B. Summary of Tungsten-Carbon Binary Results

The data obtained from differential thermal analysis and quench studies can be summarized in the tentative phase diagram of Figure 19. The heat effect observed at 2730°C for WC, and in compositions containing WC, could be caused by a phase change or by peritectoid decomposition. In the diagram, a peritectoid has been chosen because this reaction more favorably accounts for the irreversibility of the heat effect observed by DTA. The solidus shown at 2765°C is also based on DTA data. Nadler and Kempter[9] recently reported a melting temperature of 2720°C for WC. This value is lower than the 2765°C determined in these

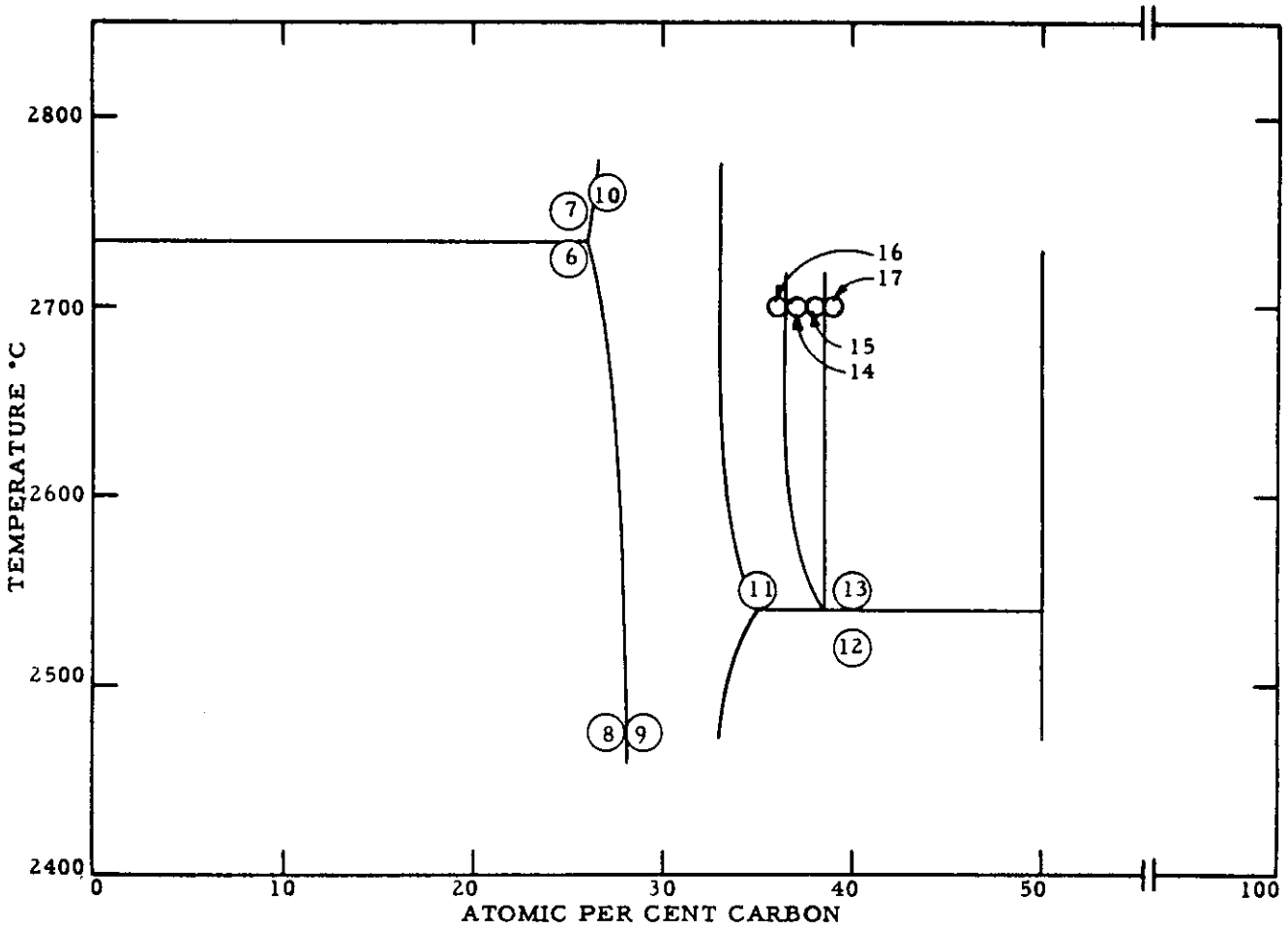


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Figure 18. - Partial Phase Diagram Indicating Datum Points Referred to in Text

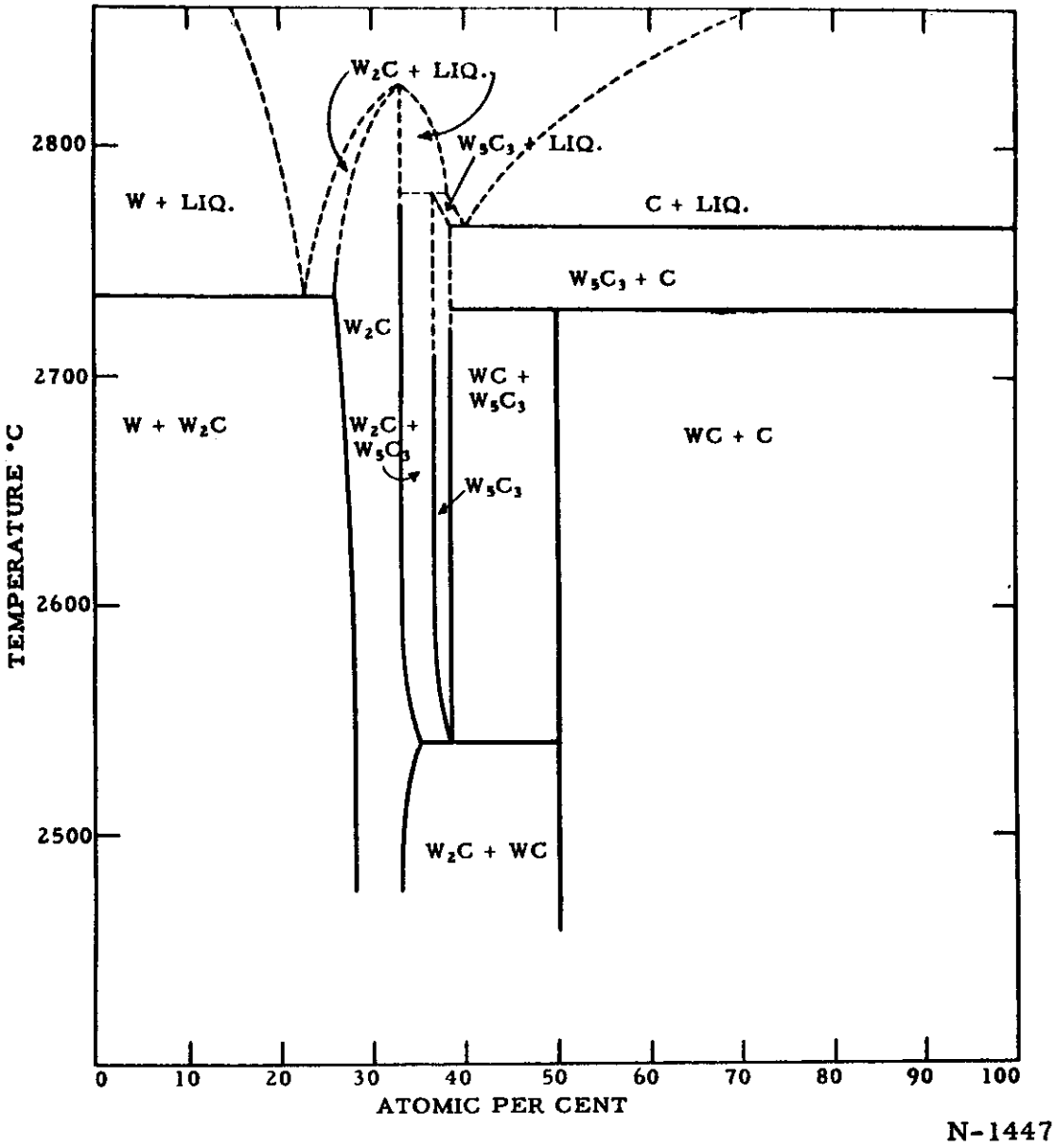

Figure 19. - Tentative W-C Phase Diagram Summarizing Experimental Data

studies but in far better agreement than the 2600°C value reported by Sykes.[4]

A compound has been found in this system which is stable above 2540°C and which has the approximate formulation W_5C_3. Carbides with this formula have not been reported previously, but there are a number of borides, germanides, and silicides of this type.[12] An example of the latter is W_5Si_3, and it is conceivable that there is a structural analogy between this compound and W_5C_3 as there is between B_4C and B_4Si.[13] The melting behavior of W_5C_3 has not yet been determined, but tentatively, it has been shown to form by a peritectic reaction.

The melting temperature of W_2C also has not been determined as yet, but on the basis of these preliminary observations, it is higher than the 2750°C reported by Sykes.[4]

Features of the tungsten-carbon phase diagram, which are now believed to be complete and accurate, can be summarized as follows:

1. The eutectic temperature between W and W_2C is 2735°C.

2. W_2C may accommodate 72 and 74 atomic per cent tungsten in the lattice at 2475° and 2735°C, respectively.

3. Carbon solubility in W_2C is only evident at 2540°C, the eutectoid temperature. There is no evidence of solution above or below this temperature.

4. A eutectoid reaction occurs at 2540°C.

5. A high-temperature compound approximating the formulation W_5C_3 dissociates at 2540°C, on cooling, into W_2C and WC. This phase could not be retained even by rigorous quenching into molten tin.

6. WC apparently dissociates at 2730°C into W_5C_3 and carbon prior to melting.

7. The solidus temperature between W_5C_3 and C is 2765°C.

IV. CONCLUSIONS

The following conclusions are drawn from the experimental work outlined in this report:

1. A tentative phase diagram for the tungsten-carbon system has been proposed from available experimental data. The system is generally more complex and is stable to higher temperatures than reported by Sykes.[4] The W_2C-WC phase region is the source of greatest discrepancy. A new carbide phase, W_5C_3, has been found to be stable above 2540°C and WC has been observed to decompose approximately 30° below its melting temperature.

2. The tungsten-carbon phase diagram will attain a stage of completion when melting temperatures and melting mechanisms for W_2C and W_5C_3 have been determined. In additon, corollary data will be obtained by visual methods to support the solidus temperature of 2765°C obtained by differential thermal analysis. These data, in the form of a completed phase diagram, will appear in Progress Report No. 7 to be issued under an extension of the present contract.

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