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ROLE OF THE BINDER PHASE IN
CEMENTED REFRACTORY ALLOYS

Report No. MAL 671/58-20
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Title of Project: Role of Binder Phase in Cemented Refractory Alloys

Object: To make a detailed study of the action of the binder phase in cemented alloys of the refractory metallic substances with the objective of explaining the several factors which control the physical and mechanical properties of the sintered parts, and to provide a basis for the proper selection of the best binder materials and sintering techniques for specific situations.

Summary: The role of the binder phase in cemented refractory alloys has been investigated with primary emphasis on the Wolfram Carbide (or Tungsten Carbide, WC)-Cobalt alloys. One aspect of the work has been to prepare a reasonably complete ternary phase diagram of the system W-Co-C. This has made it possible to show what phases exist at a sintering temperature of 1400°C. and how these phases react on heating and cooling.

The results have shown the existence of three ternary phases, namely σ which is approximately $\text{Co}_3\text{W}_3\text{C}$, θ which is approximately $\text{Co}_3\text{W}_6\text{C}_2$ and κ corresponding to the formula $\text{Co}_3\text{W}_{10}\text{C}_4$.

The phase boundaries of these single phase regions have been determined with reasonable accuracy and the two and three phase boundaries located approximately. It has been possible to show the most probably vertical section on the WC-Co line and predict the equilibrium phase relations for alloys made from WC and cobalt at various compositions and temperatures. This work has established the fact that this vertical section cannot be considered as a "Quasi binary" phase diagram, and that therefore, only a ternary diagram will furnish information regarding the number of phases and their composition during the sintering process.

It is also possible to make general predictions about the probable sequence of events during the heating and cooling cycle of the sintering operation. An important observation is that the two phase field, in which alloys having cobalt contents of commercial interest can exist as WC+ cobalt solid solution, is quite narrow and emphasizes the necessity of careful control of sintering atmosphere to prevent carburization or decarburization. A very limited amount of work has been done in replacing cobalt with nickel or iron.

A further study of the sintering mechanism has been made by observing the shrinkage or densification which takes place during the sintering operation.

A high temperature sintering dilatometer was built, capable of following the changes in length of carbide samples from room temperature to 1500°C. The visual micrometer gauge, now used, is being replaced by a continuous automatic strain recorder. The sintering furnace temperature is controlled with $\pm 2^\circ \text{C}$.

Sintering curves were determined, at a constant rate of heating from room temperature to 1500°C., for carbide samples containing from 0 to 25% Co. Isothermal sintering curves at various temperatures from 1200 to 1400 also were obtained. Sintering of carbides in the presence of other metals than cobalt has been investigated in a preliminary fashion. The results of the above experiments are now being analyzed for their theoretical significance. It is hoped that a continuous record of the linear dimensional changes during heating, cooling and isothermal holding, combined with measurements of hardness and strength, and an observation of the microstructure at room temperature, will lead to a determination of the optimum sintering temperatures, heating rates, holding periods and other related factors.

As a result of the work so far, it is possible to state what phases are desirable in a strong alloy and what ranges of compositions will yield these and only these phases. It is further possible to propose a tentative picture of the sintering mechanism which defines the role of the binder phase and indicates the physical distribution of the carbide and binder phase which would be expected to give the best strength properties. The establishment of the phase diagram has determined the conditions of the sintering atmosphere which are necessary to obtain the desirable structure.

INDEX

	<u>Page No.</u>
<u>Introduction</u>	1
I <u>The Ternary Phase Diagram W-Co-C</u>	3
General Experimental Techniques	3
The Ternary Isothermal Section at 1400°C.	6
The Intermediate Phases	7
General Observation on the Ternary Diagram	8
II <u>Dilatometric Investigation of the Sintering Process</u>	9
Description of Equipment	10
Sintering Runs at Constant Heating Rate	11
Sintering Runs at Constant Temperature	12
III <u>Conclusions and Recommendations</u>	13
The Mechanism of Sintering	13
Conclusions Concerning Carbides of Superior Properties	15

Introduction

This report represents a summary of work done in investigating the role of the binder phase in cemented refractory alloys and outlines the progress made up to the termination of the present contract. Although much has been learned, the picture is still far from a complete one and the work is to be continued under a new contract. Consequently the present discussion will include certain speculations as yet unproven and conclusions which are not yet verified completely by detailed experimental facts. It should be regarded as a report of progress.

It has been common practice for many years to prepare useful bodies from refractory metals and alloys by powder metallurgy techniques in which the powdered material was sintered together by heat treatment into strong and dense shapes. It has also been common practice to add to the refractory material a binder or auxiliary metal which lowered the temperature of sintering to a reasonable value and assisted in the process of densification. In the field of the refractory carbides, a great deal of work has been done in an attempt to find the most suitable combinations of carbide and binder for specific purposes and the commercial production of specific combinations is highly developed.

It has been clearly recognized for some time that the role of the binder phase is considerably more than just a cement or adhesive which sticks the carbide particles together, but in spite of all the work done there is still no really clear picture of the mechanism which would permit one to improve the properties of the cemented carbides except in an essentially empirical fashion. The present work was undertaken with the hope of clarifying this picture.

Efforts have been directed primarily to a study of the system of wolfram monocarbide and cobalt since these alloys are of considerable industrial importance and it was expected that principles learned from this system would be applicable to more complex alloys. The compositions of commercial interest in this system cover the range of from 5 to 25% by weight of cobalt.

In the past nearly all discussions of the behavior of this system have assumed that it was in effect a pseudo-binary system in which the phases were wolfram carbide and a cobalt rich solution. The present work has shown that in the case of compositions in the commercial range, which have been sintered to equilibrium, the assumption of a two phase alloy is probably correct but that this represents a special or limiting case. The consideration of this as a general case may be very misleading.

Actually the system must be considered as a ternary system and the section containing cobalt and wolfram carbide, while two-phase in part, actually is quite narrow and is crossed by three phase fields. This means first that if the alloy is carburized or decarburized by small amounts during sintering, the product will consist of three phases. Secondly, the intermediate stages of sintering may involve the formation of three phase alloys and thus the mechanism of sintering may be much more complex than previously believed.

As a result of these considerations, the major part of the work has proceeded along two lines. The first has been concerned with obtaining a picture of the ternary phase diagram W-Co-C in sufficient details to understand what may take place chemically during the sintering of WC-Co alloys. While there are still many points to be fixed, the important aspects of the diagram have been established. This is described in Part I of the report. The second aspect of the work has been directed toward a better understanding of the mechanism of sintering of the WC-Co alloys or rather the mechanism of densification of these alloys and is described in Part II. This has been studied principally by means of the sintering dilatometer with which it has been possible to follow in a continuous fashion the shrinkage of pressed compacts as a function of temperature and time. From an analysis of these shrinkage curves it is hoped to obtain some insight into the kinetics of the sintering process and to determine whether one or several processes are involved. The work has not yet progressed far enough to permit general conclusions to be drawn.

Part III contains a discussion of the mechanism of sintering in the WC-Co alloys and of the role of the binder phase together with the general conclusions.

Thus the work of this program has been directed toward investigating the constitution and the mechanism of sintering of the WC-Co alloys. Only on the basis of knowledge such as this can one make intelligent predictions concerning the most suitable compositions and the most effective means of processing to obtain the desired properties of the finished body.

NOTE: The nomenclature used in this report conforms to the recommendations of the Commission on Inorganic Nomenclature, International Union of Chemistry, which, at its 1949 meeting, changed the name of the element Tungsten to Wolfram.

I. The Ternary Phase Diagram W-Co-C

In order to understand the role of the binder phase in sintered alloys of wolfram monocarbide and cobalt, it is essential to know what phases exist in equilibrium with one another and how these phases react during heating and cooling. For this purpose it was considered necessary to determine a reasonably complete ternary phase diagram of the system W-Co-C.

The significant features of the three binary diagrams, W-C, W-Co and Co-C which form the boundaries of the ternary diagram have been determined by previous investigators and are given in the A.S.M. Metals Handbook, 1948 Edition. In the case of the W-C system, the phase boundaries were not given at temperatures as low as the normal sintering temperature and these boundaries have been fixed by a special precision determination which will be reported separately.

Two important studies of the ternary system have been made by Takeda⁽¹⁾ and by Brownlee⁽²⁾. While in general qualitative agreement, they differ considerably from a quantitative point of view and indicate very clearly that additional work is necessary to clarify the picture. Both investigators identified the ternary intermediate phase called eta, which includes the composition corresponding to the formula Co_3W_2C but disagree as to its composition limits. The structure of this phase has been determined by Westgren⁽³⁾. No other intermediate phases have been reported. The data on the structure of the phases known in the ternary diagram prior to the beginning of the present work are given in table I.

General Experimental Techniques

All of the alloys used in the present investigation were made from powders of wolfram, wolfram monocarbide, cobalt and carbon and were of the grade used in the manufacture of commercial cemented wolfram carbide.

The wolfram and wolfram carbide were obtained from Fansteel Metallurgical Corporation. The carbon content of the wolfram carbide was shown by analysis to be 6.15% carbon by weight.

The cobalt powder was obtained from Carboloy Company and its analysis is reported in table II.

The carbon was carbon black with very low ash content. In some cases spectrographic carbon was crushed and used as additions. No differences between these two carbons could be observed.

(1) See Table VI for Literature References

In general, the specimens had a weight of ten grams and the powders were weighed out to the nearest milligram. They were ground and mixed in small stainless steel ball mills, using balls of the same material. Benzene was used as a dispersing agent. The grinding period was usually 1 hour since this was shown to give sufficiently good mixing of the powders without too great a contamination from the mill. After ball milling, the specimens were pressed in cylindrical or rectangular dies. No paraffin or other lubricant was used and the small compacts had sufficient green strength to be handled without difficulty.

Several sintering furnaces were employed. In the high frequency furnace, Fig. 1, the specimens were placed in a tightly covered graphite crucible which was completely buried in carbon black. This produced a strongly carburizing atmosphere and also had the disadvantage that rapid and uniform cooling rates were not possible. A small molybdenum wound resistance furnace, Fig. 2 was set up to use a controlled gas atmosphere but since the activities of carbon in the various alloys was not known, it was not possible to establish in any simple way, a truly neutral atmosphere.

The most satisfactory arrangement was a vacuum furnace based on the Arsen principle which employed a graphite helix as the resistance heating element. Specimens were placed on either graphite or zirconia stands and there was generally a slight carburization of the specimen surface. The evaporation of the cobalt at a sintering temperature of 1400°C . was not significant. This furnace had a sufficiently rapid cooling rate, about 300°C in the first minute, to retain the high temperature structures. The sintering time was kept constant at 2 hrs. at temperature and investigation showed that with proper grinding and mixing, complete homogenization could be obtained in this length of time at temperature in the range of $1300-1400^{\circ}\text{C}$.

Specimens of high cobalt content were melted at these temperatures and in such cases a graphite crucible lined with magnesia cement proved satisfactory in preventing excessive carburization.

The principal methods of investigating the sintered alloys were x-ray diffraction and microscopic examination. Several modifications of the powder diffraction technique were employed, the most useful being the Perelco recording x-ray spectrometer. The use of this instrument resulted in a tremendous saving of time in the identification of phases and making an estimate of the amounts of each present. Approximate determinations of the phase boundaries was made by the disappearing phase method. When precise measurements of lattice constants were required, the symmetrical back reflection focussing camera was employed.

In the preparation of specimens for microscopic examination, the special problems of polishing arose from the combination of relatively soft and very hard phases. A transformation of the cobalt could also be induced by the polishing operations. Still another difficulty was encountered in the case of some of the ternary phases in which the specimen was very fragile and contained many pores. In general, the method of polishing described by Tarasov⁽⁴⁾ using a diamond hone proved quite satisfactory.

Previous to honing, the specimens were mounted in lucite and ground on a belt grinder with a rough carborundum belt. The hone used was a 600 grit Norton diamond hone. For hone cleaning, boron carbide of 600 grain size was used on hardened steel plate. As a lubricant kerosene proved satisfactory.

The next step of polishing was performed on a Buehler microcloth covered wheel with a Buehler Diamet-Hyprex polishing compound, grade 1, diamond particle size of 4 - 8 microns. Diamet-Hyprex fluid was used as a lubricant. For the final polishing a Diamet-Hyprex polishing compound of grade 000 (particle size of 6 - 1/2 micron) was used on a micro-cloth covered low speed wheel with the same lubricant.

This technique of diamond honing and polishing proved very good but the previous step on the carborundum belt is unsatisfactory, because the grinding causes smearing of material and long grinding times due to the fact that the grinding material is softer than the specimen. It would be desirable to use a diamond cut off wheel, which undoubtedly would yield a sufficiently good surface for honing.

The etchant used for the identification of the several phases was generally alkaline potassium ferricyanide (10 gr $K_3[Fe(CN)_6]$ and the 10 gr KOH dissolved in 100 gr of water). A cold etchant was used, because it was easier to control the etching time. For etching of two-phase cobalt wolfram carbide alloys the etching time was usually two minutes. Cobalt etches yellowish and carbide gray with a light shade to lilac. If double carbides are present the etching time must be reduced to about 1 second, otherwise heavy black tarnishing occurs. This etchant causes on the eta phase a wide scale of colors depending on etching time. The coloring effect offers a positive identification of eta.

Because the etchant mentioned does not attack the grain boundaries of cobalt, a standard ferric chloride etchant was used for some high cobalt alloys where the first precipitation of the second phase on grain boundaries was examined. The etching of these high cobalt alloys was difficult, and no entirely satisfactory method was found.

The Ternary Isothermal Section at 1400°C.

The ternary diagram was developed by first making a detailed survey of the phases existing at the 1400°C. isothermal section. This data was then combined with the known information on the three binary diagrams and with additional data which is gradually accumulating based on x-ray, microscopic and thermal analysis. The combination, of course, must be made in accordance with the theoretical principles which determine phase reactions in alloy systems. Fig. III shows the isothermal section at 1400°C. while Fig. IV is the basal section of the ternary diagram at room temperature.

The aspects of principal interest in the 1400° isothermal section are first the terminal phases of the line connecting Co and WC. These are the cobalt solid solution phase (β) and the wolfram monocarbide WC which are the equilibrium phases of normally sintered compositions. Of next interest are the intermediate ternary phases η , (η) which has previously been reported and θ and κ which have not been observed prior to the present work. The boundary phase W_2C may also take part in the sintering process under certain circumstances.

There is considerable disagreement in published work as to the extent of solubility of Co in WC, and estimates vary from 30% to practically zero at the eutectic temperature. The limit is difficult to determine since small amounts of Co in a Co + WC mixture are not revealed by x-rays. An attempt was made to show the extent of solubility by the precise measurement of the lattice constants of pure WC as compared to a preparation of WC + 5% Co, rapidly cooled from approximately the eutectic temperature. The values obtained, using copper radiation, were:

$$\text{Pure WC} \quad - \quad a = 2.9060 \text{ \AA} \quad c = 2.8371 \text{ \AA}$$

$$\text{WC} + 5\% \text{ Co} \quad - \quad a = 2.9060 \text{ \AA} \quad c = 2.8370 \text{ \AA}$$

Even though the sizes of W and Co atoms are nearly the same, this excellent agreement must mean that the solubility is quite small.

The solubility of WC in Co, considered as a quasi-binary situation has been investigated on several occasions and these results are in agreement on the fact of an increasing solubility with increasing temperature but the values of maximum solubility varies between 5 and 16 per cent by weight. An attempt was made to determine this value more exactly. This involved the preparation of a series of alloys lying on the Co-WC line of the diagram which were melted and quenched from the neighborhood of the eutectic temperatures. The specimens were then homogenized at 1200, 1100 and 1000°C. and examined microscopically for the appearance of the second phase. The results

were complicated by several difficulties. In the first place the "pure" cobalt showed the existence of a second phase, probably the stable cobalt oxide. Secondly, the possibility of decarburization of the specimens complicates the interpretation. The results have been reported in detail by B. Levinger⁽⁵⁾ and are shown schematically in Fig. V. The significant features of the result are that the maximum solubility of the carbide is approximately 17% and that the microstructures indicate that at 1000°C. the first phase to precipitate from the solid solution is not WC but is eta. At higher temperatures the second phase formed appears to be WC. The interpretation of these results, however, is questionable and has not clearly established the conditions under which the eta phase or WC is precipitated from the cobalt corner of the diagram. The investigation was started on what now seems to be a mistaken premise, namely, that Co and WC formed a quasi-binary system. The cobalt corner of the diagram must be carefully reinvestigated and it seems desirable to choose series of alloys in which the carbon content varies systematically but the ratio of cobalt to wolfram remains constant.

The Intermediate Phases

The intermediate phases which have been observed in the W-Co-C system are of interest in establishing a complete ternary diagram but from the practical viewpoint, they are important as structures to avoid in the final product. This is because they appear to be very brittle or perhaps fragile and probably are detrimental to the strength properties of the alloy.

The eta phase, as seen in Table I has cubic symmetry and includes the composition $\text{Co}_3\text{W}_3\text{C}$. Its structure and atom positions have been determined by Westgren⁽³⁾ and isomorphous phases are formed when iron or nickel replace the cobalt. At present, the melting point of this phase is not known nor is it certain how its composition boundaries change with temperature. Limited evidence indicates that this change is small. Brownlee⁽²⁾ investigated this phase but it appears that he did not differentiate clearly between eta, theta, and kappa. A comparison of his range and that found in the present work is shown in Fig. VI. Fig. XI illustrates the microstructure of this phase in a high Co alloy.

The theta phase, whose composition corresponds to $\text{Co}_3\text{W}_6\text{C}_2$ is also of cubic symmetry and its structure must be closely related to the eta structure. The lattice constant is 11.25 Å and the unit cell is face centered cubic. The order of the diffraction lines is similar but the relative line intensities are different. It should be possible to place the atoms in this structure but this work is not contemplated in the near future.

The kappa phase has a very narrow range of homogeneity and corresponds to the approximate formula $\text{Co}_3\text{W}_{10}\text{C}_4$. Its diffraction pattern is quite different from eta and theta and its structure is unknown at present. It seems, however, as if the structure of these three phases may be related in that they form a progression from eta to W_2C and that the clue to the structure of kappa may be found in this relationship. The theta and kappa phase have not been reported in the literature prior to the present work. The diffraction patterns of these double carbides are shown in Table III and Fig. VII.

In the temperature range of about 1400°C . these intermediate phases can be formed readily by solid diffusion of the constituent powders, Co, WC, and W and this formation is accompanied by a slight expansion, leaving quite porous and fragile specimens. Upon heating to higher temperatures, however, in the range of 1700 to 1800°C ., considerable shrinkage takes place and relatively dense and fairly strong specimens are obtained. Thus diffusion and densification are not synonymous in these alloys.

General Observations on the Ternary Diagram

Although a large amount of data has been obtained, it is far too little to establish the complete ternary diagram. However, it has been possible to obtain a tentative model. A photograph of this model is shown in Fig. VIII. The actual position of the liquidus and solidus lines can be placed only approximately but certain limiting conditions can be fixed. It is possible to show, as in Fig. IX the probable projection of the liquidus lines and indicate what sorts of transformation may take place.

The nature of the diagram may be visualized by considering the possible form of the vertical section of the diagram drawn through the cobalt-WC line. Since the surfaces of the diagram cut this vertical section at very oblique angles, a small displacement of the corners of the three phase fields causes a considerable change in the appearance of the vertical section. On the basis of the thermal analysis and the microscopic work done so far it is clear that the "quasi binary" section cannot be correct. Figs. X and XI illustrate the effect of excess or deficiency of carbon on the phases present in a high cobalt alloy, leading to the appearance of free graphite or of the carbon poor eta phase. The most probable vertical section seems to be section E of Fig. XII although undoubtedly this will have to be modified somewhat as more experimental data is obtained. If the WC-Co system cannot be treated as a "quasi binary" more than two phases must be involved in any reaction between WC and Co, even if the composition of the alloy as a whole lies in the two phase field. The solubility relationships and the number and composition of participating phases can only be known if the ternary equilibrium diagram is determined.

II Dilatometric Investigation of the Sintering Process

This part of the project is concerned with the investigation of the sintering mechanism of the refractory alloys WC-Co. Although good sintered carbide parts are produced industrially, very little is known about the phenomena that take place during the heating and cooling cycle. The industrial heat treatment is carried out in a neutral or reducing atmosphere. A linear shrinkage of 12 to 20% occurs. The shrinkage is accompanied by a certain amount of grain growth, the fine grains tend to disappear and the larger ones become coarsened. Sintering temperatures are usually within the range of 1350° to 1500°C.

It is known that a liquid phase forms between 1300 - 1350°C., even below the melting point of cobalt, and that this liquid phase consists of a solution of wolfram carbide in the cobalt binder. The superiority of cobalt over other binder materials is attributed to the high solubility of WC in Co at high temperatures, and its relative insolubility at low temperatures, so that on cooling, the carbide precipitates from the binder upon the existing grains.

Some experimental work on the mechanism of sintering has been reported in the literature. By leaching out the binder material with acid, Dawihl and co-workers(6) showed that a continuous skeleton of carbide exists in an alloy of 6% Co after sintering at temperatures as low as 900°C. In fully sintered specimens the skeleton becomes more and more discontinuous as the binder content increases over 10%. Below 10% Co the coefficient of expansion of the sintered carbide varies only little with increasing binder contents. Above 10% Co it eventually becomes equal to the cumulative expansion of the constituents. Dawihl reports that WC-Co alloys can be completely sintered at a temperature as low as 1250°C., if given a sufficiently long time. Mantle(7) examined the effect of the sintering temperature upon the properties of sintered carbides. He concludes that 1305°C. is the lowest temperature at which sintering can be carried out; it is therefore dependent upon the presence of a liquid phase. Some dilatometric studies of the sintering process were undertaken at Krupp in Germany (8). The curves (shrinkage vs. temperature) were not evaluated in detail, but they indicate that shrinkage begins at 900 - 1000°C., and attains greatest speed at barely 1400°C. The slope of the shrinkage curve increases with cobalt content. Sandford and Trent(9) also followed the shrinkage during sintering. They observed the sample through an optical pyrometer and reported that contraction starts at approximately 1150°C. and is complete at approximately 1320°C. for Co contents of 6 and 10.5%. They conclude that sintering commences before a liquid phase appears, but is not complete until after it is present.

A great number of problems concerning the role of the binder are still unsolved. Some of them are here noted:

- a) Is the shrinkage producing force due to the attraction between the carbide particles themselves, or to the surface tension of pores, or to other factors?
- b) Is the presence of a liquid phase essential for complete densification?
- c) Is a skeleton of carbide particles formed during heating to temperature, at the sintering temperature, or on cooling?

It is thought that an investigation of these problems will lead to a better knowledge of the sintering process, an important factor in the production of better carbides.

Description of Equipment

The dilatometric method was selected because it is able to supply information on the sintering process, while it happens, at any temperature or time during the heating cycle. A sintering dilatometer was therefore built. It consists of a closed end 'McDaniel' High Temperature Refractory porcelain tube, 18 in. long, 0.5 in. internal diameter, into which the pressed sample is inserted. The sample is a bar of the following dimensions: 1" x 1/4" x 1/4". The tube stands vertically in the furnace, the sample supports a synthetic sapphire rod which transmits its expansion or contraction to an 'Ames' micrometer gauge attached to the top of the porcelain tube. The gauge is graduated in 0.001 in. and has a range of 0.5 in.

This assembly is inserted into a vertical tube furnace where the sample is in the constant temperature region of the furnace. Approximately 6" of the dilatometer tube protrudes from the furnace so that the dial gauge is essentially at room temperature. The joints, from furnace to tube, and from tube to gauge, are water cooled rubber compression seals to assure gas tightness. The temperature of the sample is measured by a platinum - platinum rhodium thermocouple, protected from the reducing atmosphere of the furnace by a porcelain tube. The thermocouple is part of the temperature control system which consists of a variable transformer regulating the power input, a potentiometer by means of which the temperature can be measured, and an electronic temperature controller which maintains a constant temperature by activating a relay which inserts a resistance into the heating circuit. Most of the equipment used is shown in Figs. XIII and XIV.

Separate gas atmospheres can be provided inside the furnace and inside the dilatometer tubing, if the experimental conditions require it. Usually, 'Forming Gas' (20% H₂ and 80% N₂) is used in both. It protects the molybdenum winding of the furnace and the sample from oxidation without being as subject to the danger of explosion as pure hydrogen would be. Oxygen and water are removed from the gas by passing it over heated copper chips and through 'Drierite' drying reagent. To prevent decarburization of the sample, small graphite rings are introduced into the tube; their direct contact with the specimen is prevented by a small refractory spacer ring.

The measured temperature is checked periodically by a reference thermocouple, inserted in place of the sample into the dilatometer tube. This thermocouple is standardized against the melting points of gold and silver. Although the temperature can be maintained constant within $\pm 2^\circ\text{C}$. over a period of days, the absolute temperature is known only to within the inherent accuracy of the thermocouple and measuring potentiometer, approximately $\pm 5^\circ\text{C}$.

At first, a thin, hollow porcelain tube was used as a dilatometer rod, but, at high temperatures, a small amount of irreversible bending occurred. It was replaced by the synthetic sapphire rod, now in use, which stands up very well at the temperatures in question. The dilatometer system is standardized by means of a one inch long piece of metal, usually wolfram, the thermal expansion of which is known. From such a standardization run, the expansion and contraction with temperature of the porcelain and sapphire parts can be calculated, and this correction is applied to each sintering run.

The present set-up requires the operator to read and record the position of the pointer of the micrometer gauge, the accuracy of the results depending greatly upon the frequency of such readings. A continuous recording system is now being installed. It consists of a 'Schaevitz' linear differential transformer activated by the motion of the sapphire dilatometer rod. The transformer indicates a mechanical position electrically, the electrical impulses are fed through an amplifier-rectifier, to a 'Brown' recording potentiometer, which draws a continuous record of change of length versus time at temperature. This arrangement is shown in the block diagram of Fig. XV.

Sintering Runs at Constant Heating Rate

A series of samples, containing from 0 to 100% cobalt, were heated at a constant rate (10° per minute up to 1000°C., 5° per minute from 1000° to 1500°C.). The changes in length were plotted against temperature; a typical curve is shown in Fig. XVI. Table IV summarizes the experimental data. Specimens of binder contents from 1 to 15% have curves very similar in shape and range. The sample first expands on heating, shrinkage becomes noticeable at 800°C., becoming increasingly more rapid up to 1300°C. - 1350°C. at which

temperatures shrinkage is completed. Further heating produces a slight expansion. On cooling, the sample shrinks linearly with temperature. With increasing amounts of Co, from 1 to 15%, the net amount of linear shrinkage increases from 17 to 19.3%. Shrinkage is incomplete with cobalt contents of less than 1%. A sample containing 25% cobalt did not support its own weight and deformed at high temperatures. The sintering of pure cobalt is completed at 950°C., and that of wolfram carbide is insignificant even at 1500°C., less than 1% linear shrinkage. Similar experiments with copper, iron, and nickel binders (5% binder + 95% WC) showed, respectively, 4.6, 11, and 12% shrinkage.

Sintering Runs at Constant Temperature

Isothermal dilatometer curves, shrinkage versus time, were taken for various compositions at temperatures from 1200°C. to 1400°C. The set of curves corresponding to a binder content of 7.5% is reproduced in Fig. XVII. Table V indicates the time required to reach the final length at various temperatures, also the total holding time of each sample at temperature. After reaching the indicated dimension the sample did not shrink any further during the remaining time at temperature.

These curves are to be correlated with mechanical tests and with microscopic examination of the structures of the specimens.

The purpose of these experiments is to find a mathematical representation of the rate of shrinkage and the variation of shrinkage rate with temperature and with composition. It is hoped that the experimental data can be fitted to a theoretical shrinkage mechanism.

III Conclusions and Recommendations

The Mechanism of Sintering

Many details of the sintering mechanism are still obscure but the results to date make it possible to present a tentative picture of the process. Starting with the intimate mechanical mixture of WC and cobalt, the first effect of heating is the tendency of the cobalt particles themselves to sinter. This takes place in the range of 800 - 1000°C. and probably accounts for the strengthening observed in the commercial presintering operation. Very little densification occurs in this temperature range. There may be some solution of WC in the surface of the cobalt grains.

As the temperature is raised to the vicinity of 1200 to 1250°C., the solubility of WC in cobalt increases both in rate and in amount and some densification is observed. At this temperature and after long periods of time, approximately one half of the total possible shrinkage can be obtained.

Somewhere in the region of 1300°C. the most highly saturated portions of cobalt begin to melt and the solubility of the liquid phase increases rapidly. Since this solubility is at the expense of the WC grains, the smallest grains and the sharp points of the larger grains are dissolved first. This permits the remaining grains to rearrange themselves, the pores diffuse outward and marked densification of the specimen takes place. The driving force for densification is the strong surface tension of the liquid binder and its tendency to eliminate the pores.

If the temperature is maintained at about 1350°C., the liquid phase rapidly reaches saturation with WC. However, the equilibrium is not complete since the solubility depends upon the radius of curvature of the WC surfaces, and wolfram and carbon are dissolved from the points and redeposited on flat surfaces. This process is complicated by the fact that deposition is markedly preferential in WC, certain crystallographic planes being favored and the growing grains have a characteristic angular appearance with flat faces rather than a spherical shape. Thus at the sintering temperature, the liquid phase acts as a sort of transfer agent for moving WC from points of grains to surfaces and from small grains to larger grains. After about 1 hr. sintering, for instance, the grains are of more uniform size and somewhat larger size than the original WC powder. All of this rearrangement combined with the high interfacial tension acts to eliminate the pores and densify the specimen.

While at temperature, there seems to be very little direct sintering of WC grains to one another. The chief evidence for this is the fact that the specimens at temperature are plastic and have little strength.

If the temperature is now reduced, the liquid phase starts to precipitate WC and at the freezing point, since the solubility drops from about 35% to about 10% WC, a considerable amount of WC is deposited. The existing WC grains must nucleate this precipitation and it is believed that the precipitated WC develops the contact areas between the grains and thus forms the strong skeleton of carbide. The strength of a carbide specimen from which the cobalt has been dissolved is the principal evidence for the existence of such a carbide skeleton.⁽⁶⁾

From the freezing point down to room temperature, the solid solubility of WC in cobalt decreases somewhat and there exists the possibility of precipitation and consequent hardening of the binder phase by this process. At present there is no microscopic evidence of such precipitation within the volume of the cobalt grains and some preliminary experiments on cobalt rich alloys have indicated no significant changes in hardness.

From the above it can be seen that the binder phase must play several roles in determining the final properties of the sintered carbide alloy. In the first place, it is necessary for maximum densification to have a binder phase which is molten at the sintering temperature. Secondly, the surface tension of the molten binder phase must be high in order to provide the forces which densify the compact and expel the pores. Thirdly, the binder phase should have a high solubility for WC when molten and a rather low solubility when solid so that it provides a large reservoir of WC which can be precipitated to form a strong carbide skeleton. In addition, the decreasing solid solubility with decreasing temperature offers the possibility of improving the physical properties but it is not clear at present that this constitutes an appreciable contribution.

The importance of the actual adhesion between the binder phase and the WC surfaces is still open to question. If it is true that the principal contribution to the strength of the cemented alloy comes from the strong carbide skeleton, then this adhesion may play a very minor role. The very marked "cratering" action observed on cemented wolfram carbide cutting tools suggests that this adhesion is rather weak. By the same token, if the strong carbide skeleton is of prime importance, the actual mechanical properties of the binder phase would be expected to be relatively unimportant. The elastic modulus of the skeleton is very much higher than that of the binder phase and because of its brittleness the skeleton would be broken when deformation takes place before the properties of the binder would have an opportunity to make themselves felt.

On the other hand, the presence of a binder phase is an essential feature of the cemented carbide from a different point of view. The carbide is brittle and thus undoubtedly very notch sensitive. The skeletal structure is, of course, largely made up of notches. If the pores of the skeleton are completely filled with binder, it seems as if the stress concentrations at the carbide grain boundaries would be considerably reduced and the strength of the cemented alloy, at least as measured by a transverse bend test would be increased.

The definite superiority of cobalt as a binder metal over nickel and iron is a matter of considerable interest. At present it seems as if this difference is directly related to the solubility of WC in the molten binder as compared to the solubility in the solid, that is, the amount of WC which is precipitated during freezing and is used in building up the strong bonds of the skeleton. It appears that the phase diagrams of WC with nickel and iron are essentially similar to that with cobalt, but that the solubility of WC in the binder metal increases in the order of Cu, Fe, Ni.

Conclusions Concerning Carbides of Superior Properties

On the basis of the work done up to the present time, certain conclusions can be drawn as to the conditions which must be fulfilled in order to prepare cemented wolfram carbides of superior properties.

There are variables entering into the actual production of cemented wolfram carbide articles which have been recognized in commercial production as being important. These include the production of the original WC powder, its size and size distribution, the variables involved in the milling, the distribution of cobalt, conditions due to pressing and the like which have not been investigated as a part of the current program. Successful combinations of these variables have been worked out by the several carbide manufacturers.

The present work has shown that the most desirable structure for a cemented wolfram carbide is a two phase structure consisting of WC grains and the cobalt rich solid solution binder phase. The ternary phase diagram has indicated that this two phase field is narrow and that even small amounts of carburization or decarburization lead to the presence of other phases in the structure which are undesirable. This emphasizes the importance of a very careful control of sintering atmosphere. If the economic aspects are disregarded it appears as if vacuum sintering or sintering in an inert gas offers certain advantages in this direction.

The conclusions concerning the desirable phase content of the cemented alloy place very definite restrictions upon possible ranges of composition. The alloys should lie in the WC-Co two phase field of the diagram and the range of cobalt content between about 5 and about 15% by weight. A binder content lower than 5% does not supply enough precipitated WC to form strong bonds in the skeleton and values higher than 15% result in the beginning of a discontinuous carbide skeleton with a consequent decrease in strength.

The fallacy of adding metallic wolfram to the composition in the hope of strengthening the binder phase is obvious since this simply moves the alloy into the three phase field, WC + eta + liquid, which is undesirable. The only possible reason for adding wolfram would be to counteract some carburization during sintering and it seems better to prevent this rather than try to compensate for it.

The use of nickel to replace part of the cobalt in the binder should not be overlooked as a possibility, particularly in view of the fact that nickel appears to accelerate the diffusion and permit more rapid homogenization. If the presence of nickel does not reduce the solubility of the binder for WC, it might have a beneficial effect and this aspect should be investigated further. Most other elements added to the cobalt appear to reduce the solubility for WC or wolfram and carbon in the liquid state.

If the two phase structure is the correct one, then the only variables at the control of the experimenter are the binder content and the extent of the skeleton formation between the carbide grains. Even small binder contents (less than 5%) will permit a close packed carbide skeleton in which the interstices are completely filled with binder. As the proportion of the binder increases, the number of junctions between carbide particles must decrease but at the same time a greater quantity of carbide is precipitated on freezing and the fewer bonding points become stronger. Thus there are two opposing tendencies at work as the binder content increases and the strength should show a maximum. At this highest strength one could not expect any degree of ductility because the carbide bonds would break and the failure would be catastrophic.

With higher binder contents, the carbide bonds become fewer, but perhaps stronger and the carbide skeleton becomes more and more tenuous, perhaps forming islands of strong skeleton in the binder matrix which are only occasionally bonded together. Here it would be expected that the properties of the binder itself would begin to play a role and some measure of ductility observed by the breaking of a few carbide bonds but without complete failure. The properties then would be strongly dependent upon the state of aggregation of the carbide.

Thus it appears that if cemented carbides of superior quality are to be prepared, one must know on the one hand exactly what combination of properties is desirable while on the other hand one must understand completely the mechanism of sintering because only in this way can proper distribution of the carbide and binder as well as the most favorable carbide bonding be achieved.

TABLE OF CONTENTS

<u>Tables</u>	<u>Figures</u>		<u>Page</u>
I		Structure of Phases of the Ternary Diagram W-C-Co	1
II		Chemical Analysis of Cobalt (FM 122 Carboloy)	1
	I	High Frequency Furnace	2
	II	Vertical Tube Furnace - Molybdenum Wound	3
	III	Co-W-C Isothermal Section at 1400°C.	4
	IV	Co-W-C Isothermal Section at Room Temperature	5
	V	Co-WC Quasi Binary Results	6
	VI	Single Phase Fields of Co-W-C	7
III		Planar Spacings and Relative Intensities of Reflection: η , θ and K Phases	8
	VII	a) Powder Diffraction Patterns of η and θ Phases b) Powder Diffraction Patterns of K and WC Phases	9 10
	VIII	Tentative Model of Ternary Diagram Co-W-C	11
	IX	Co-W-C Diagram, Projection of Liquidus Lines	12
	X	WC and Graphite Needles in Co Matrix	13
	XI	Eta Phase Dendrites and WC Grains in Co Matrix	13
	XII	Possible Vertical Sections Co-WC in Co-W-C diagram	14
	XIII	Sintering Dilatometer	15

TABLE OF CONTENTS

<u>Tables</u>	<u>Figures</u>		<u>Page</u>
	XIV	Sintering Dilatometer and Auxiliary Equipment	16
	XV	Components of Continuous Dilatometer Recorder	17
	XVI	Sintering Curve, Constant Rate of Heating	18
	XVII	Effect of Time and Temperature on Shrinkage	19
IV		Sintering Runs at Constant Rate of Heating	20
V		Isothermal Shrinkage	20
VI		Literature References	21

TABLE I

Approx. Formula	Lattice Type	Lattice Constant, A.			No. of atoms/cell	Space. Group.
		a	c	c/a		
Co	F.C.C.	3.545	—	—	4	$O_h^5 - F_{m5}$
	Hex. C.P.	2.507	4.072	—	2	$D_{6h}^4 - C^6/mC$
W	B.C.C.	3.158	—	—	2	$O_h^9 - I_{m5}$
C(graphite)	Hex.	2.456	6.696	—	4	$D_{6h}^4 - C^6/mC$
Co_7W_6 (d)	Rhomb.	8.95		$\alpha = 30.41^\circ$	13	
W_2C	Hex.	2.995*	4.727*	—	3	
WC	Hex.	2.906*	2.837*		2	
Co_3W_3C (η)	F.C.C.	11.04*	—	—	112	$O_h^7 - Fd3m$

*Specific parameter values were measured during the present work.

TABLE II

Chemical Analysis of Cobalt (PM 122 Carbonyl)

Per cent by weight

Co - 98.6	C - 0.045
Fe - 0.07	Mn - 0.05
Ni - 0.28	Si - 0.15
Cu - Trace	S - 0.044
	O - 0.83



Figure 1

High Frequency Furnace

From Right to Left: Optical Pyrometer, Furnace, Regulating Induction Coil

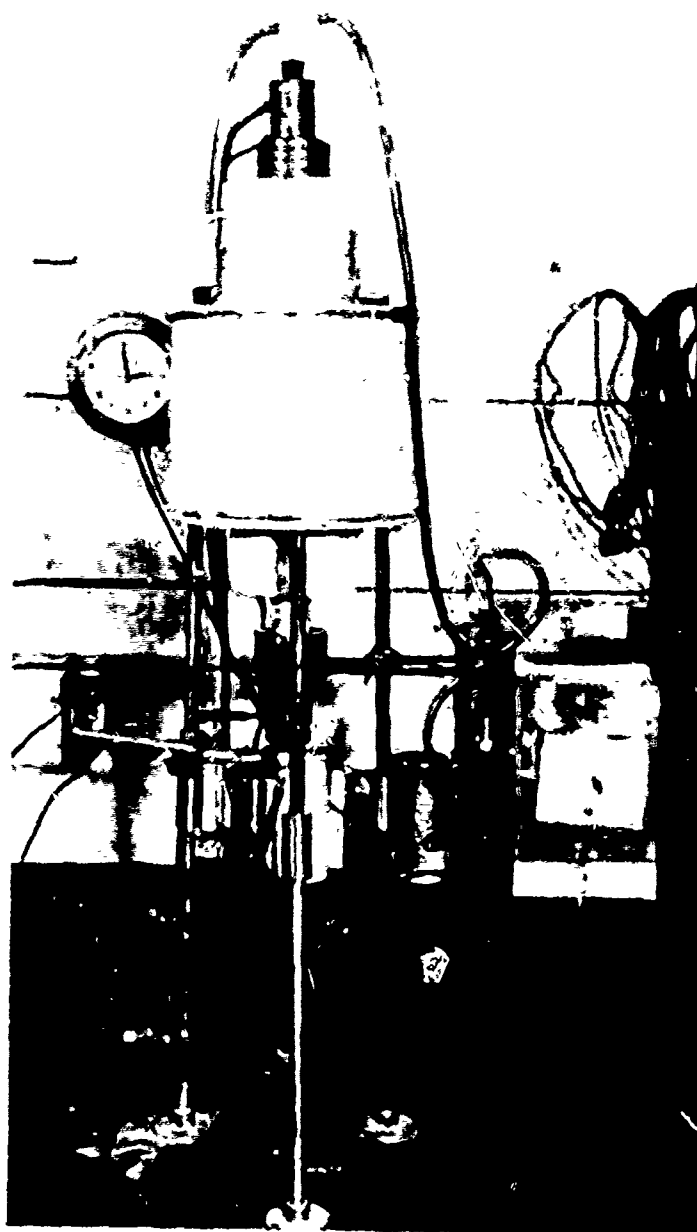


Figure II
Vertical Tube Furnace
Molybdenum Wound

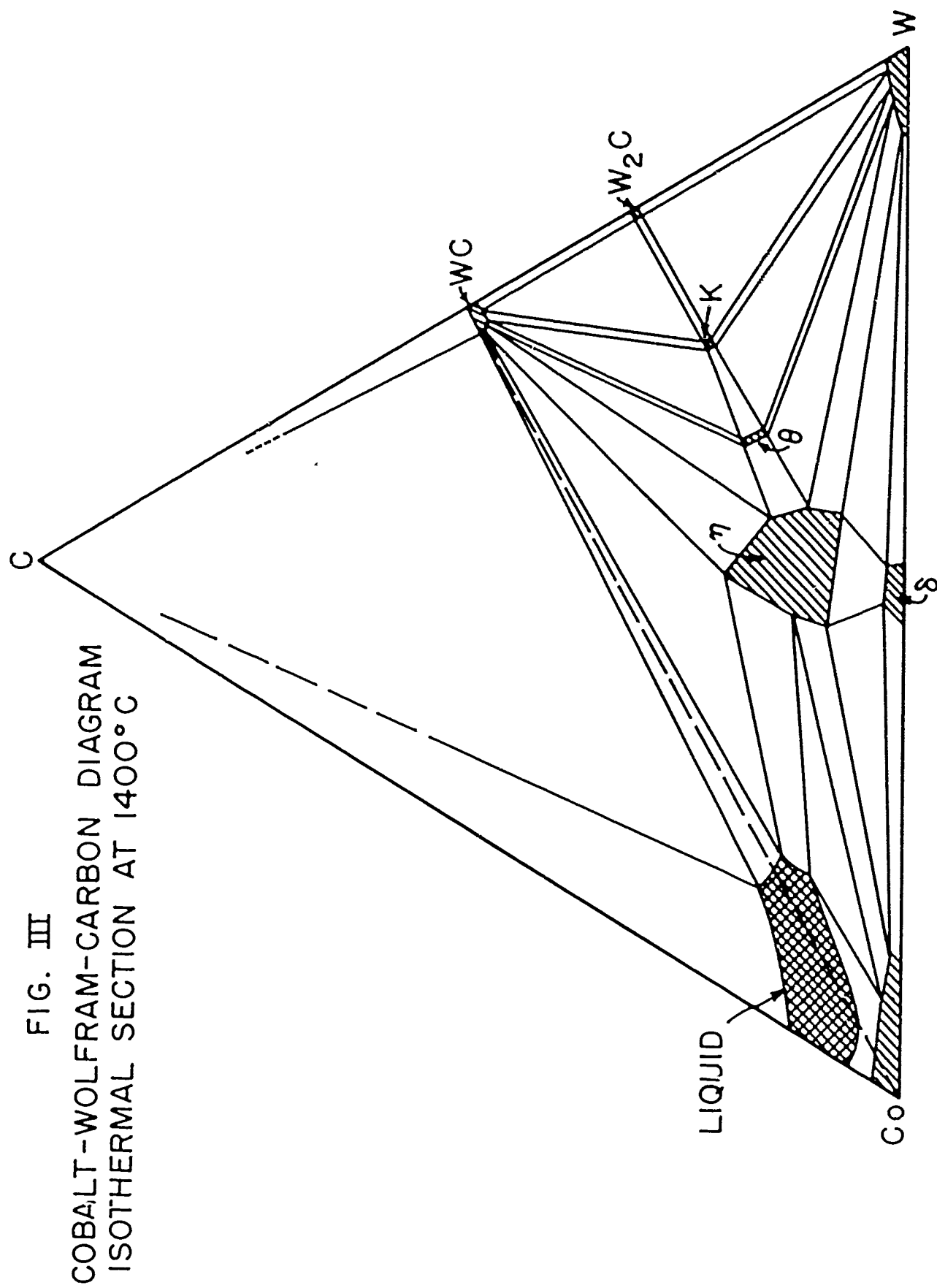
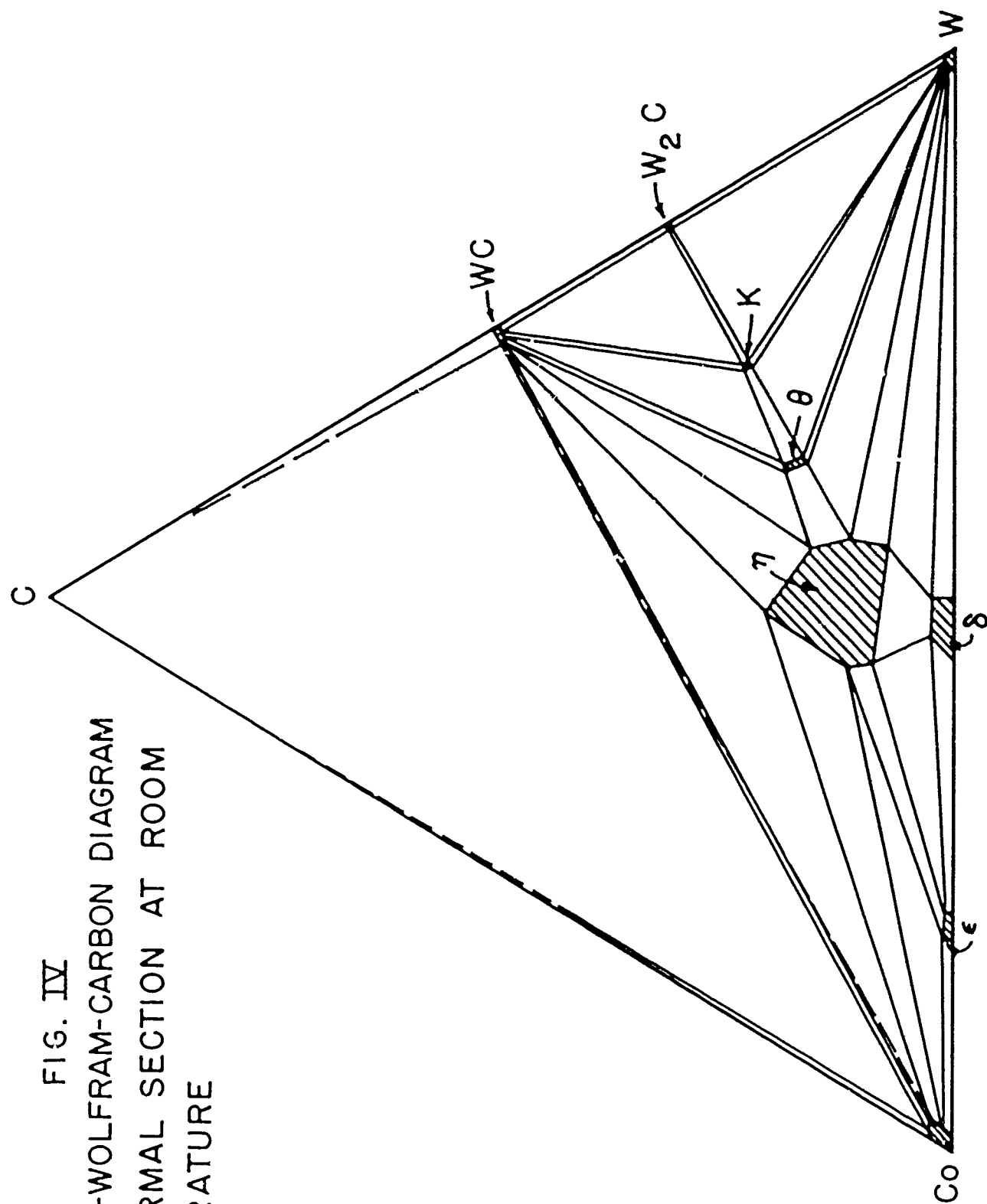


FIG. IV
COBALT-WOLFRAM-CARBON DIAGRAM
ISOTHERMAL SECTION AT ROOM
TEMPERATURE



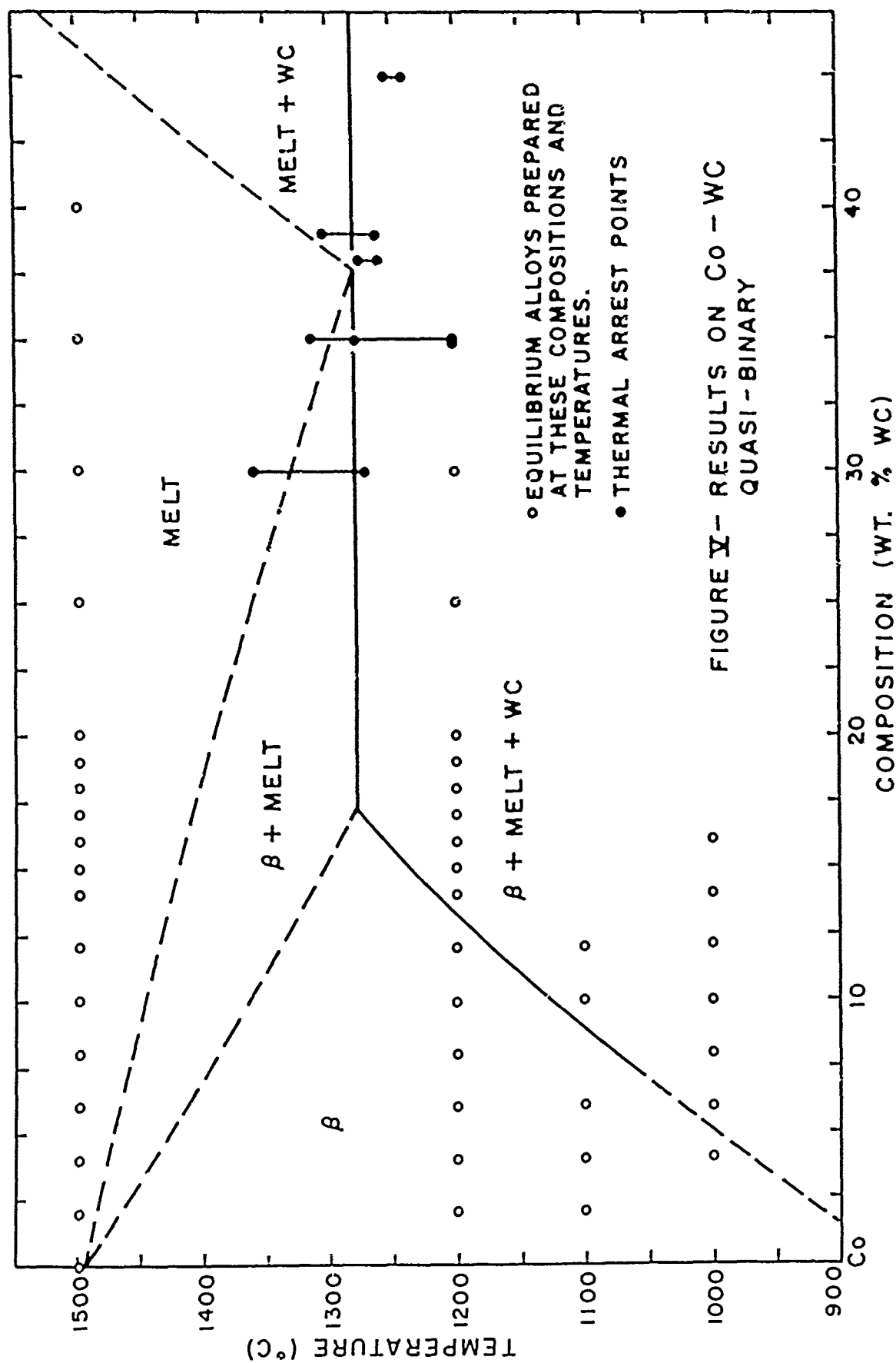


FIGURE V- RESULTS ON Co - WC
QUASI-BINARY

FIG. VI
SINGLE PHASE FIELDS OF
COBALT - WOLFRAM - CARBIDES

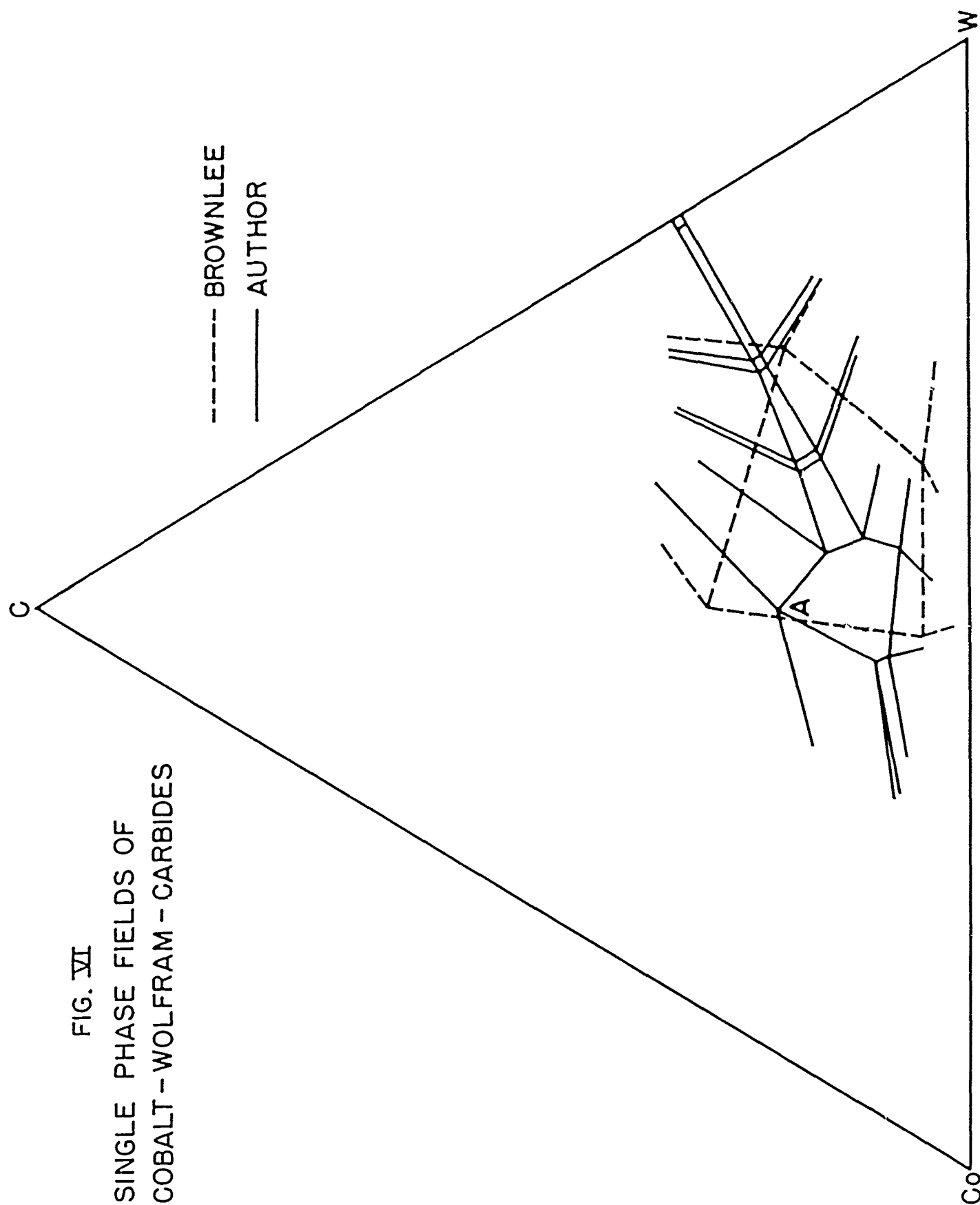


TABLE III

Planar Spacings (d) and Relative Intensities (I) of Reflections

 η , θ and κ - phases

η phase*			θ phase**			κ phase**	
<u>hkl</u>	<u>d</u>	<u>Relative Intensity</u>	<u>hkl</u>	<u>d</u>	<u>Relative Intensity</u>	<u>Spacing</u>	<u>Relative Intensity</u>
400	2.740	.24	400	2.813	.09	(d)	I
331	2.514	.36	331	2.581	.41		
420	2.450	.00	420	2.516	.00	3.34	.10
422	2.237	.65	422	2.296	.51	3.12	.14
511,333	2.109	1.00	511,333	2.165	1.00	2.57	.75
440	1.937	.50	440	1.989	.44	2.45	.80
						2.27	.36
						2.18	.59
						2.15	1.00
						2.08	.57
						1.96	.36
						1.84	.10
						1.76	.18
						1.70	.27
						1.56	.15
						1.43	.23
						1.36	.25
						1.34	.56
						1.31	.35
						1.29	.50

* In equilibrium with θ

** Average values, because this phase has very limited solubility.

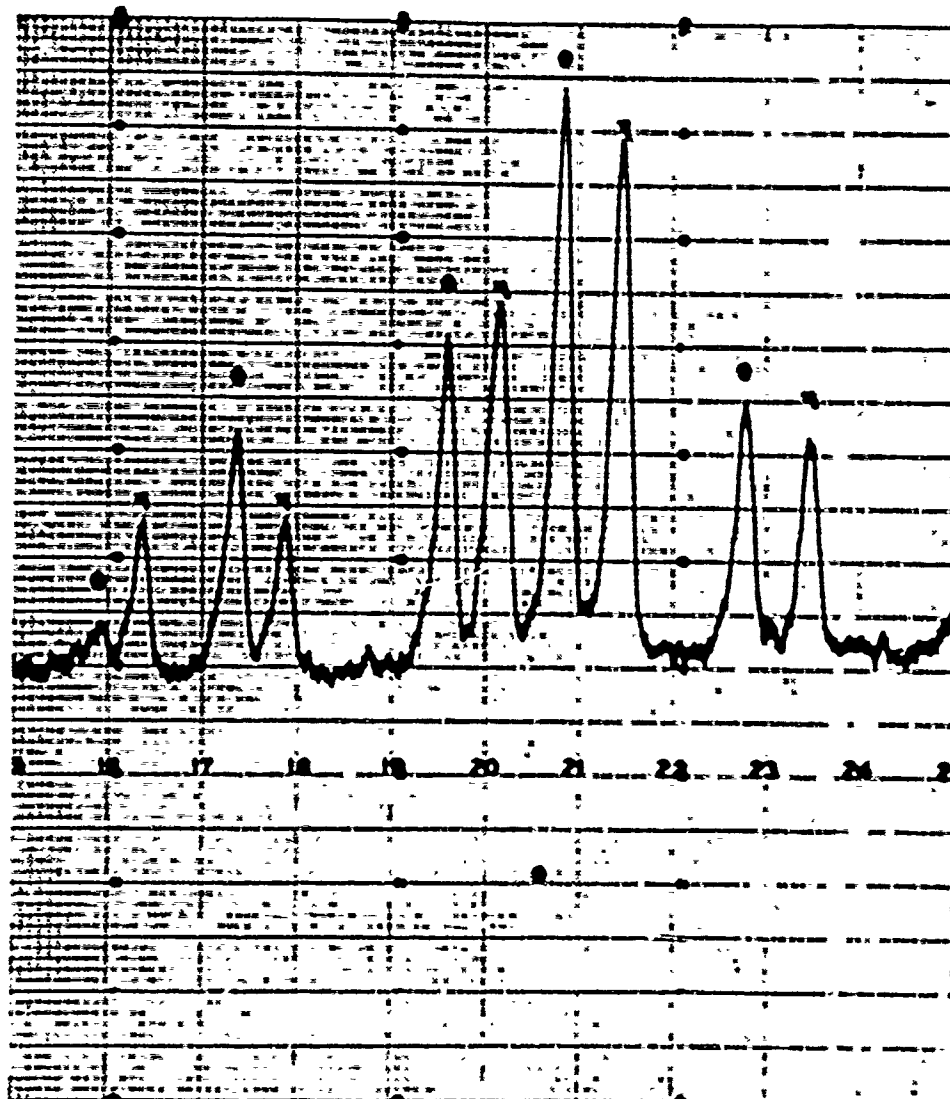


Figure VII (a)
Powder Diffraction Patterns of γ and θ phases

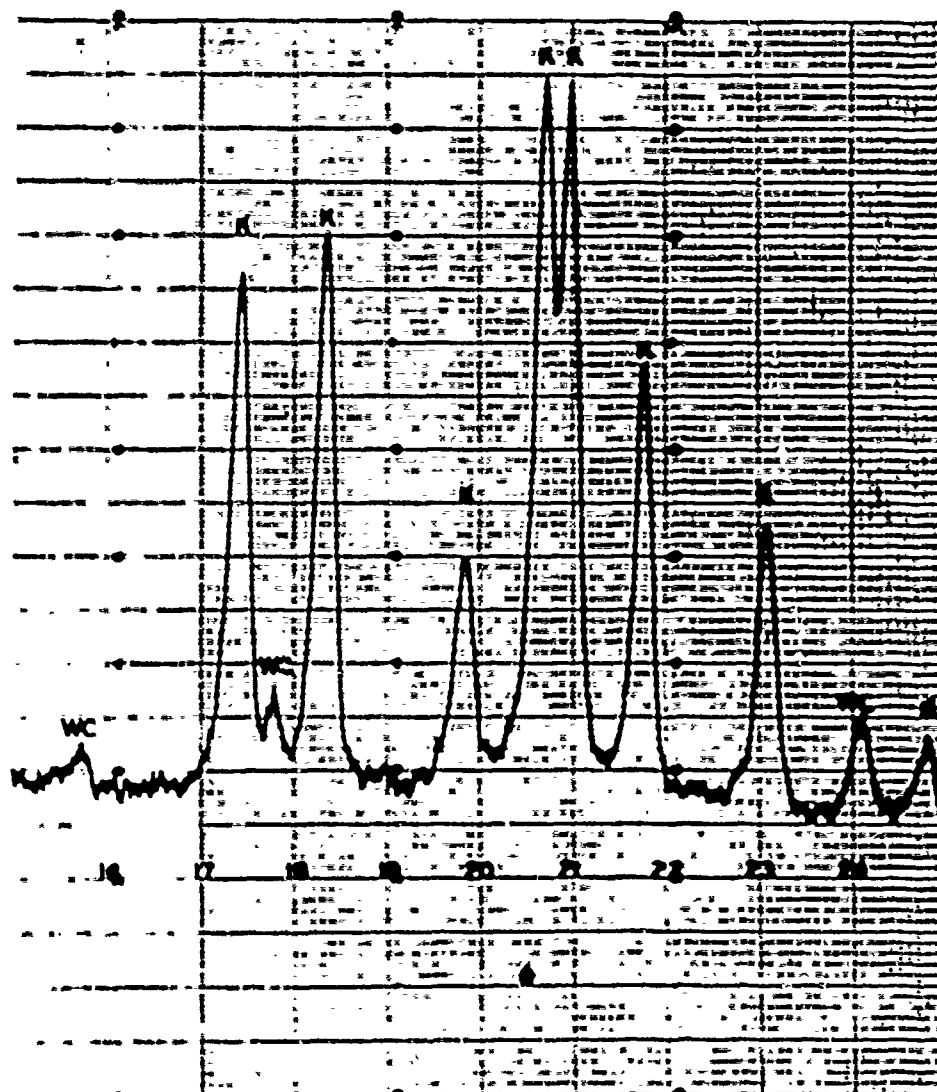


Figure VII (b)

Powder Diffraction Patterns of K and WC phases

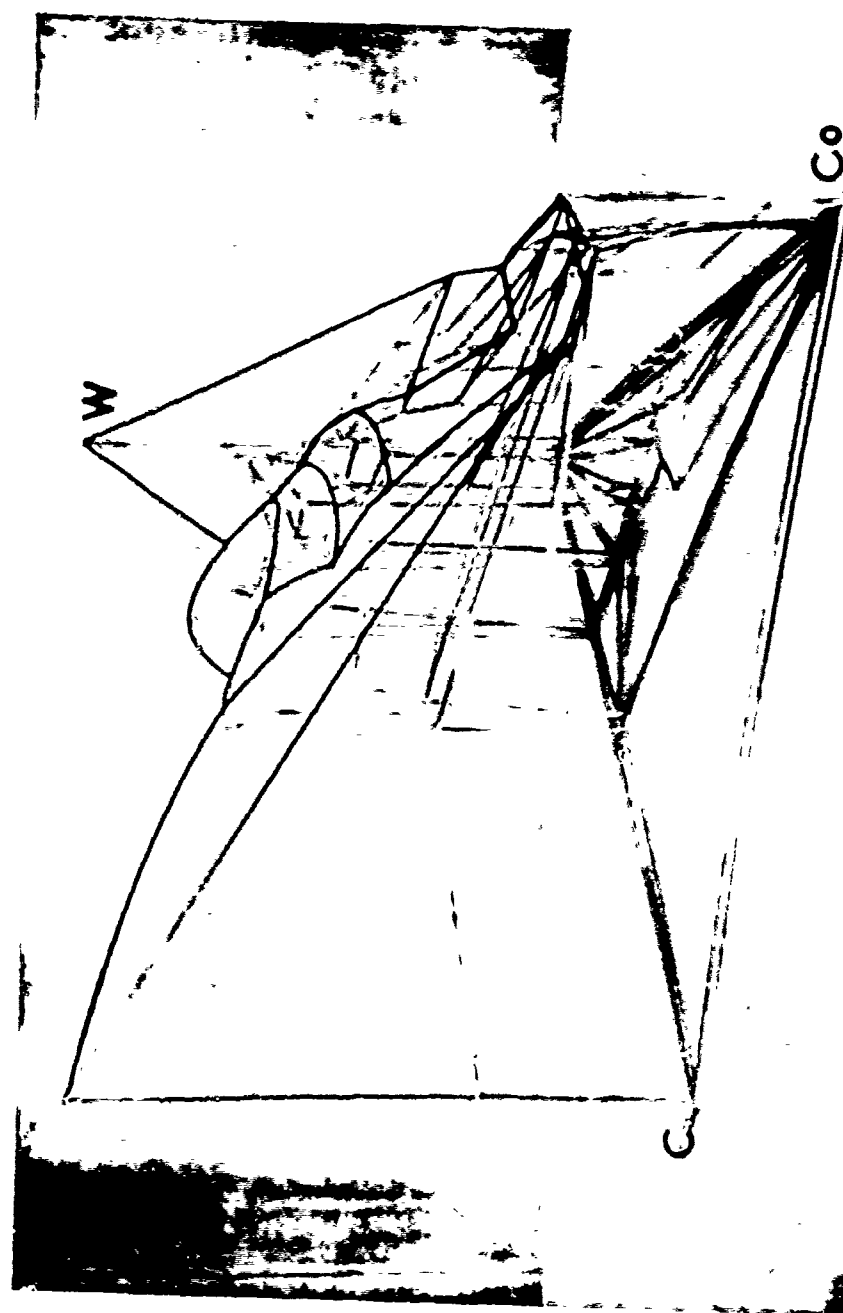
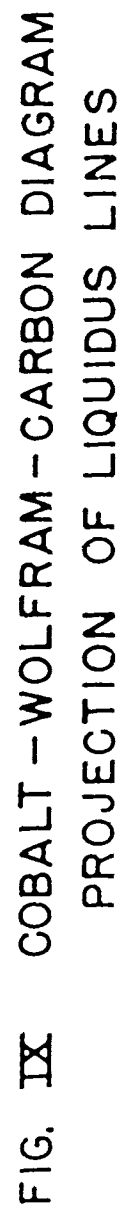


Figure VIII

Tentative Model of Ternary Diagram Co-Ni-C

$$\begin{array}{l}
 P_1: L + C \longrightarrow WC \\
 E_1: L \longrightarrow WC + W_2C \\
 E_2: L \longrightarrow W_2C + W \\
 P_2: L + W \longrightarrow \delta \\
 E_3: L \longrightarrow Co + \delta \\
 E_4: L \longrightarrow Co + C \\
 P_3: L + W_2C \longrightarrow WC + K \\
 P_4: L + W_2C \longrightarrow W + K
 \end{array}$$


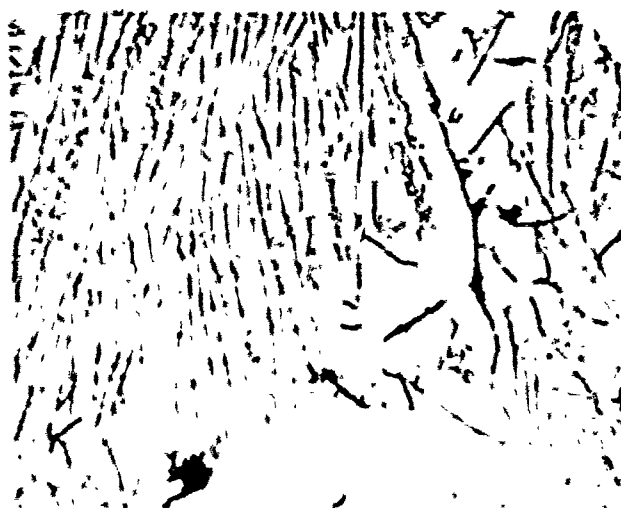


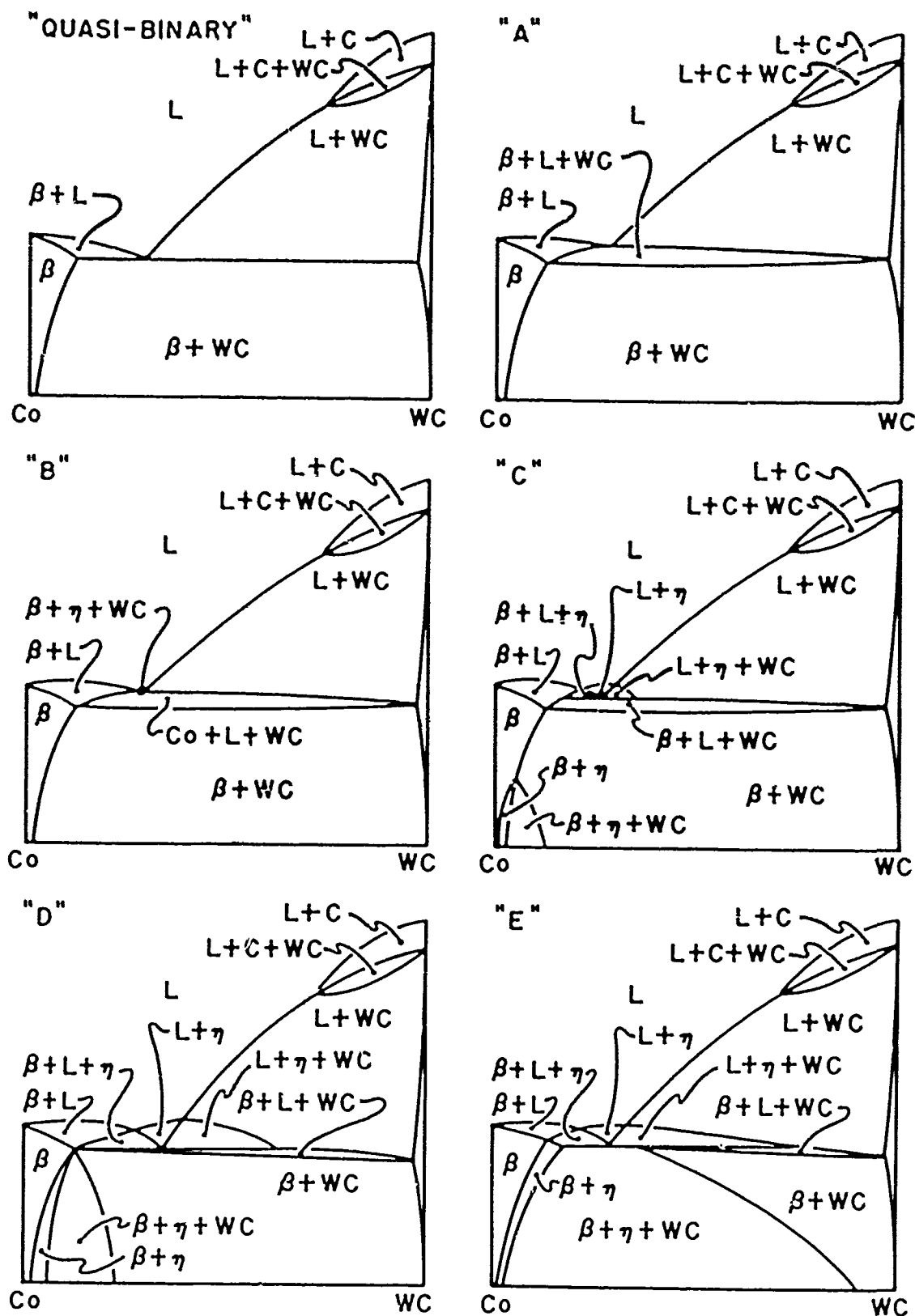
Figure X

Wolfram carbide and graphite needles in Co matrix
Composition of alloy 76.5 at. % Co, 8.5 at. % W,
15 at. % C. Furnace cooled from melt (1450°C.) $\times 250$



Figure XI

Eta phase dendrites (black) and Wolfram Carbide grains
in Co matrix.
Composition: 40% WC, 60% Co. Furnace cooled from melt
(1500°C.). $\times 1500$ approx.



POSSIBLE VERTICAL SECTIONS Co-W-C IN Co-W-C DIAGRAM.
"QUASI-BINARY" SECTION IS THEORETICALLY INCORRECT.

FIG. XII

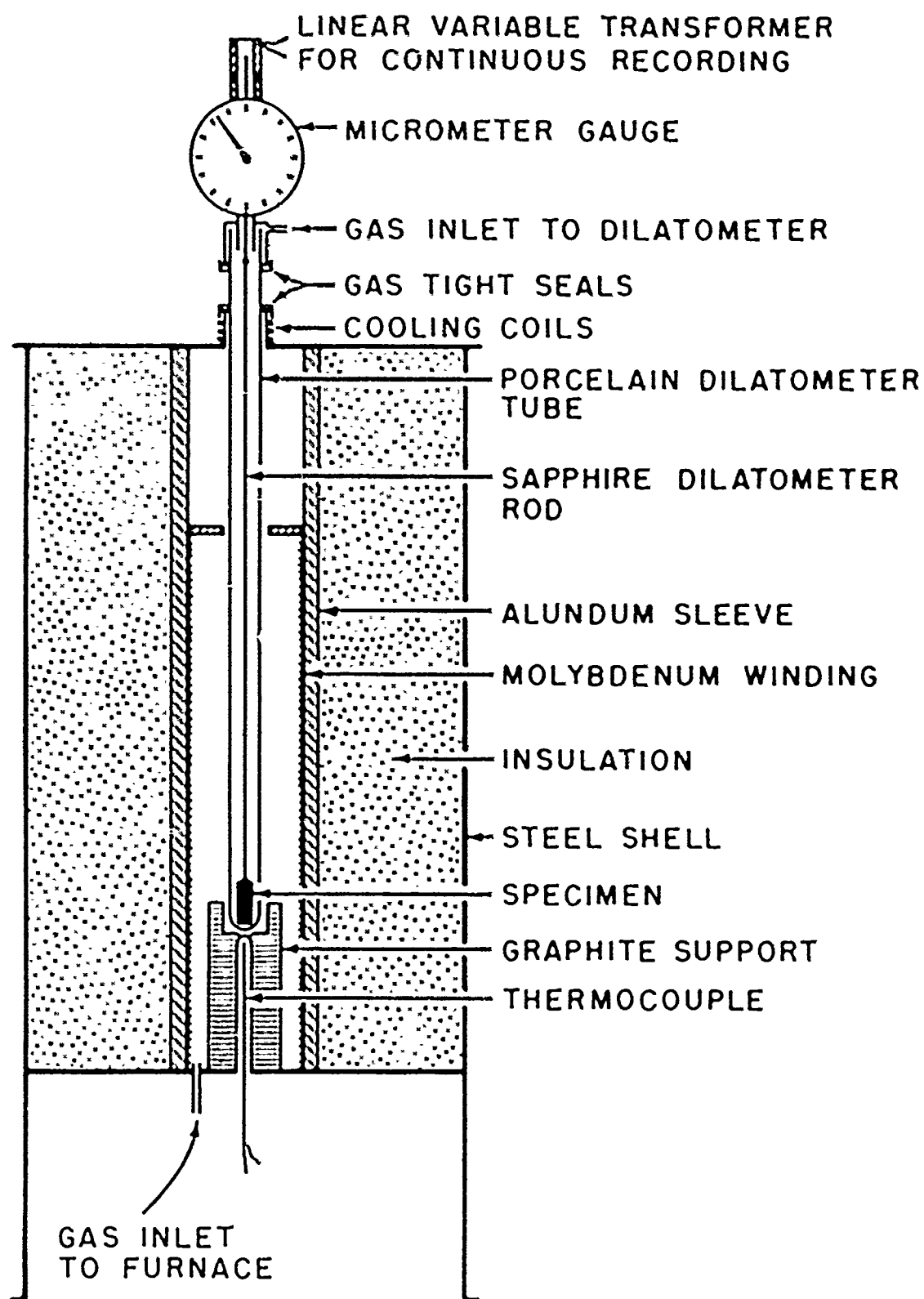


FIG. XIII
SINTERING DILATOMETER

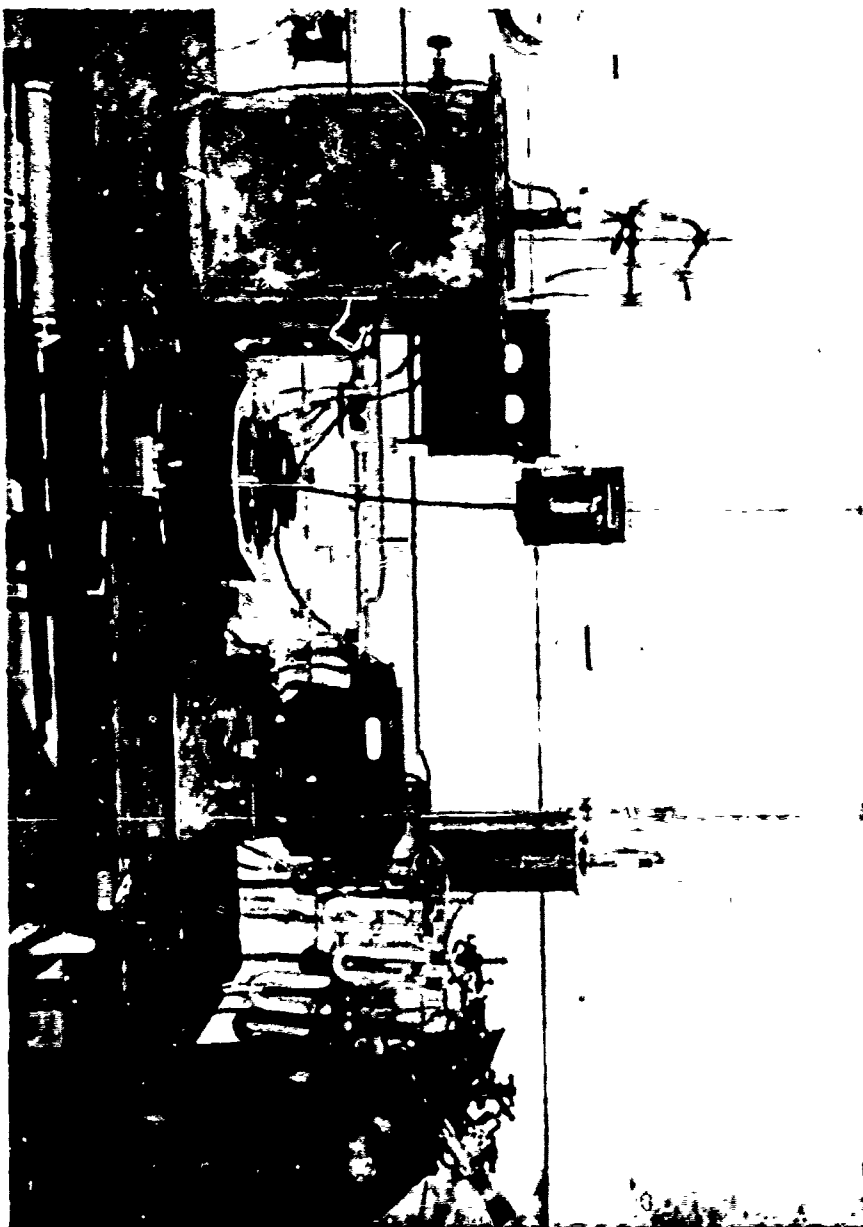
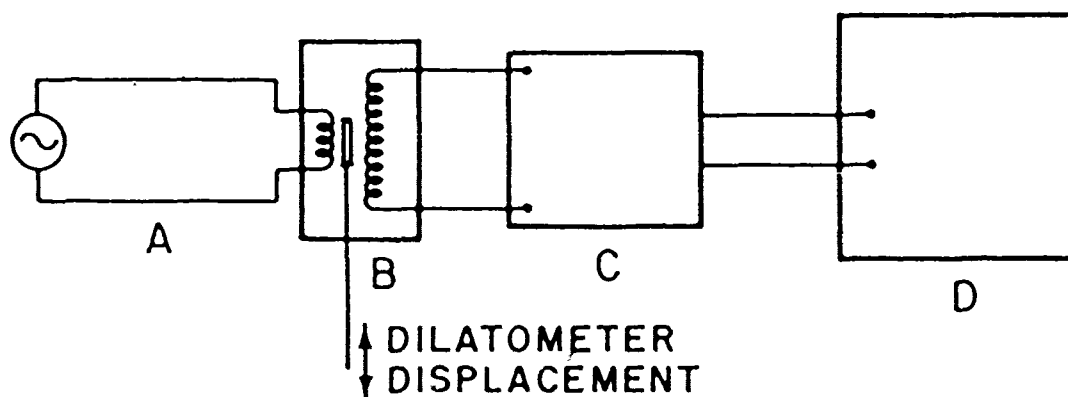


Figure XIV

Sintering Dilatometer and Auxiliary Equipment

From Left to Right: Sintering Dilatometer, Variable Transformer, Potentiometer and Temperature Controller, Gas Purification Train.



- A- 10V 60 CYCLES AC SOURCE
- B- LINEAR VARIABLE DIFFERENTIAL
TRANSFORMER (SCHAEVITZ COIL)
- C- LINEAR AC AMPLIFIER - RECTIFIER
- D- BROWN POTENTIOMETER RECORDER

FIGURE XV-COMPONENTS OF CONTINUOUS
DILATOMETER RECORDER.

FIG. XVI

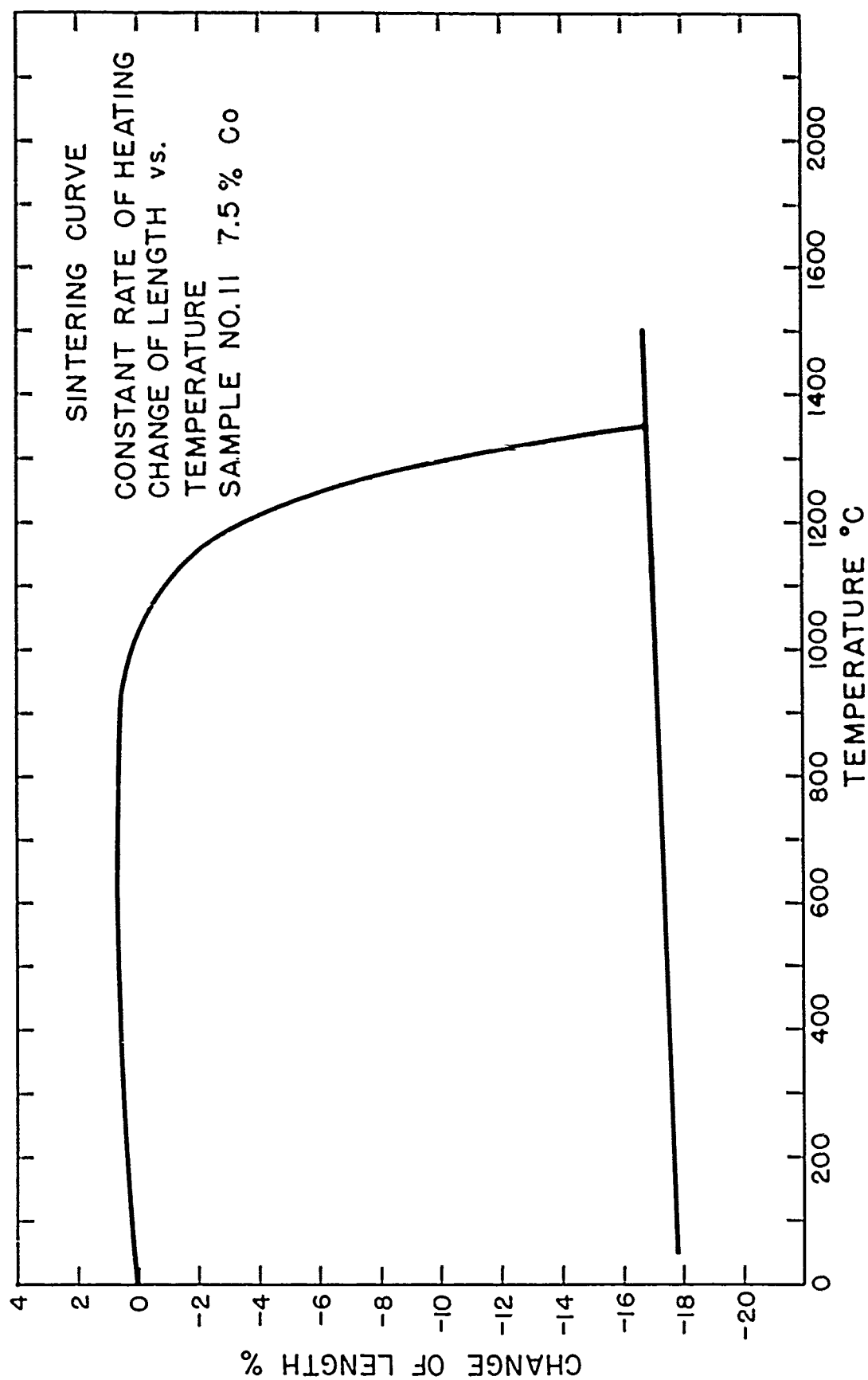


FIG. XVII
EFFECT OF TIME AND TEMPERATURE ON SHRINKAGE
SAMPLE NO. 19 7.5% Co

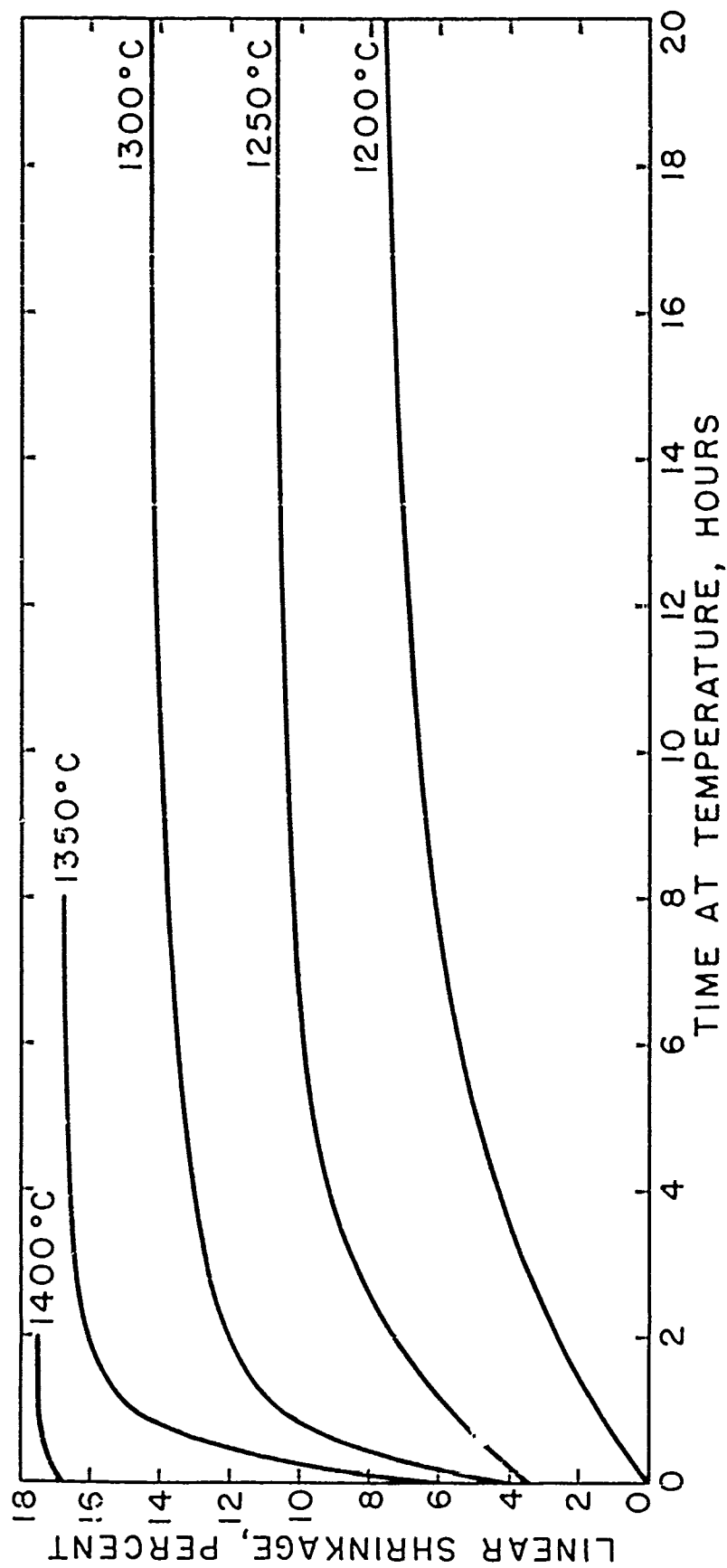


TABLE IV

Sintering Runs at Constant Heating Rate

Cobalt Content %	0.5	1	5	7.5	10	12.5	15
Linear Shrinkage %	1.6	17.1	16.9	16.8	17.6	18.0	19.3
Start of Noticeable Shrinkage, °C.	800	800	800	800	800	800	800
End of Rapid Shrinkage °C.	—	1350	1350	1350	1300	1300	1300

TABLE V

Isothermal Shrinkage

Sample No. 19

7.5% Co

Temperature °C.	Time Required for Maximum Shrinkage HRS	Maximum Shrinkage Percent	Total Time at Temperature HRS
1200	—	8.3	28.5
1250	—	13.4	144
1300	47	14.9	70
1350	5	16.7	8
1400	0.75	17.5	2

TABLE VI

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