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AFML-TR-66-181

THE SYSTEMS  
PLATINUM-CARBON AND IRIDIUM-CARBON

M. Hoch and S. K. Rhee  
University of Cincinnati

TECHNICAL REPORT AFML-TR-66-181

JUNE 1966

Air Force Materials Laboratory  
Research and Technology Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

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**THE SYSTEMS**

**PLATINUM-CARBON AND IRIDIUM-CARBON**

**M. Hoch and S. K. Rhee  
University of Cincinnati**

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## FOREWORD

This report was prepared by the University of Cincinnati, Cincinnati, Ohio under USAF Contract No. AF 33(615)-9048. This report was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736004, "Special Problems in Materials Physics." The work was administered under the direction of the Thermal & Solid State Branch, Materials Physics Division, Air Force Materials Laboratory with Mr. P.W. Dimiduk acting as project engineer.

This report covers the period of work conducted from September 1963 through August 1965. This manuscript was released by the author(s) May 1966 for publication as an KTD Technical Report.

This technical report has been reviewed and is approved.



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#### ABSTRACT

The eutectics in the Pt-C and Ir-C phase diagrams were studied in this investigation. Both systems are of a simple eutectic type with very limited solid solubility of carbon. The eutectic point of the Pt-C system exists at  $16.8 \pm 1.0$  at. ( $1.23 \pm 0.09$  wt.)%C and  $1705^\circ \pm 13^\circ\text{C}$ , and that of the Ir-C system at  $29.0 \pm 1.0$  at. ( $2.49 \pm 0.12$  wt.)%C and  $2150^\circ \pm 22^\circ\text{C}$ , respectively.

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## I. INTRODUCTION

Recently, a great deal of interest and effort has been devoted to controlling the oxidation of graphite at high temperatures by means of surface coatings with refractory metals such as platinum and iridium. To gain a better indication of possible reaction between such coatings and the graphite, this study was undertaken to investigate the eutectic temperatures and compositions of the binary systems Pt-C and Ir-C, solid solubility of carbon in both metals, and also, possibly the liquidus on the carbon-rich side of the binary phase diagrams.

Platinum and iridium belong to Group VIII of the periodic chart of the elements as do the iron group metals. Like  $\gamma$ -Fe,  $\beta$ -Co, and Ni, they also have the face-centered cubic structure. Since they have been known to react with carbon with a resulting lowering of the melting point, it would be expected that they might form eutectics with carbon as do the iron-group metals. However, such investigations have been difficult to carry out because of the high melting points of platinum and iridium, and the resulting reactions of the metals with the container material.

Literature data of the eutectics of the iron-group metals with carbon are given in Table I<sup>1</sup>. It can be noticed that the eutectic

TABLE I. Literature Data of the Metal-Carbon Eutectics of the Iron-Group Metals

Element	Atomic Number	Metallic Radius $\text{\AA}$ <sup>2</sup>	Eutectic Composition	Solid Solubility of Carbon at Eutectic Temp.
			at.%C	at.%C
$\gamma$ -Fe	26	1.263	17.1	8.79
$\beta$ -Co	27	1.256	12.75	4.5
Ni	28	1.246	10.0	2.7

composition of carbon decreases with increasing atomic number, and the solid solubility of carbon decreases with decreasing metallic radius. If this trend were also true with Pt and Ir, the carbon content of the Pt-C eutectic point would be less than that of the Ir-C eutectic, and the solid solubility of carbon in Pt would be higher than that in Ir since the atomic number and the metallic radius of Pt are greater than those of Ir.

## II. PREVIOUS INVESTIGATIONS

### 1. Platinum-Carbon System

Molten platinum, like all other metals of the platinum group, has been found to dissolve carbon which precipitates on cooling in the form of graphite. Carbon contents of 16.5 at. (1.2 wt.)% and 19.29 at. (1.45 wt.)% were found to be dissolved in molten platinum by H. Hempel and by M. Moissan, respectively,<sup>1</sup> but they failed to indicate the temperatures of the melt.

L. J. Collier, et al.<sup>3</sup> found that platinum melted at  $1730^{\circ} \pm 3^{\circ}\text{C}$  (corrected to conform with the International Temperature Scale<sup>4</sup>) when it was heated in a graphite container. This melting temperature was  $39^{\circ}\text{C}$  lower than that of pure platinum, and the resulting microstructure showed primary graphite in a eutectic-like matrix. The eutectic composition was estimated to be 16.5 at. (1.2 wt.)%C. They also found no evidence of formation of a carbide. As the lattice parameter of the metal matrix was slightly larger than that of pure Pt, the solid solubility of carbon was estimated to be about 4 at. (0.25 wt.)%C. E. Raub and G. Falkenburg<sup>5</sup>, however, found that the solubility of carbon in solid Pt was low and did not lead to a measurable change in lattice parameter. M. R. Nadler and C. P. Kempter<sup>6</sup> reported that the eutectic temperature is  $1736^{\circ} \pm 13^{\circ}\text{C}$ , and E. Rudy, et al.<sup>7</sup> reported that the eutectic temperature is  $1732^{\circ} \pm 20^{\circ}\text{C}$ . Literature data of the eutectic are summarized in Table II.

TABLE II. Literature Data of the Pt-C Eutectic

Eutectic Temperature Reported, °C	Eutectic Composition Reported, at. %C	Investigators
1730 ± 3	16.5	Collier, et al. <sup>3</sup>
1736 ± 13		Nadler and Kempter <sup>6</sup>
1732 ± 20		Rudy, et al. <sup>7</sup>

The most reliable value of the melting point of pure platinum is 1769° ± 0.9°C according to D. R. Lovejoy.<sup>8</sup>

## 2. Iridium-Carbon System

A. A. Hasapis, et al.<sup>9</sup> carried out an experiment of vapor pressure of pure iridium in a graphite container, and found that near the melting point of Ir the vapor pressure of iridium was reduced from one to two orders of magnitude by the presence of carbon, indicating that there was either reaction between carbon and iridium, or extensive solution formation. According to M. R. Nadler and C. P. Kempter<sup>6</sup>, iridium melts at 2296° ± 16°C in the presence of carbon, and E. Rudy, et al.<sup>7</sup> recently reported that the eutectic temperature is 2320° ± 20°C. On the other hand, J. M. Criscione, et al.<sup>10</sup> found that the eutectic temperature is much lower than the above data, being at 2110° ± 25°C, and this large discrepancy was explained by the slow rate of carbon diffusion in iridium. They also estimated from their metallographic observations of the samples that the eutectic concentration of carbon was not more than 5 wt. (45.7 at.) %C, and they could not detect any formation of carbides between iridium and carbon, using a high temperature x-ray diffraction camera up to 2300°C. The above literature data of the eutectic are summarized in Table III.

TABLE III. Literature Data of the Ir-C Eutectic

Eutectic Temperature Reported, °C	Eutectic Composition Reported, at. %C	Investigators
2296 ± 16		Nadler and Kempter <sup>6</sup>
2320 ± 20		Rudy, et al <sup>7</sup>
2110 ± 25	<45.7	Criscione, et al. <sup>10</sup>

A generally accepted value of the melting point of pure iridium is 2443° ± 3°C.<sup>11</sup>

In summary, all the previous investigations gave limited information on the eutectic compositions and also better temperature data are needed.

### III. PROCEDURE AND EQUIPMENT

The approach used in determining the eutectic temperatures was to heat thin pure metal pellets embedded in graphite powder and placed in a graphite container in a graphite crucible. After a heating run at a fixed temperature for a certain period of time, the metal sample was visually examined for evidence of melting, and the lowest melting point was taken as the eutectic temperature.

The graphite crucible was inductively heated in a large water-cooled copper vacuum chamber, 1 ft. in diameter and 1.5 ft. high. A schematic picture of the furnace is given in Fig. 1. A 25 kw. induction generator supplied power to the furnace, and the vacuum was maintained at less than  $10^{-5}$  mm Hg. by a Duo-Seal forepump in series with a 4 in. oil diffusion pump. The vacuum was measured with a hot cathode ionization gauge.

The dimensions of the graphite crucible were  $7/8$  in. high and  $5/8$  in. diameter with a chamber  $11/16$  in. deep, the diameter of which was  $7/16$  in. The dimensions of the graphite container were  $3/8$  in. in diameter and  $5/16$  in. high with a chamber of  $1/4$  in. diameter and  $1/4$  in. deep. A graphite lid with  $1/20$  in. diameter hole was put on the crucible in order to secure black-body conditions for temperature measurements. The graphite container and crucible were made of spectroscopic purity graphite rod.

The temperature of the crucible was read through a glass window in the top of the furnace using a calibrated Leeds and Northrup disappearing filament type optical pyrometer. True temperature was obtained after correction for absorption by the glass window which was protected from the vapors by means of a shutter.

In order to determine the eutectic compositions, samples of compositions in the eutectic range were prepared from metal powder and graphite powder. The components of the sample were weighed, mechanically mixed in a mortar with pestle, and cold-pressed into a pellet in a steel mold under a pressure of 50000 psi. The pellet was cylindrical in form with a 3/16 in. diameter usually weighing 0.5 g. This pellet was placed on a graphite plate in the graphite crucible described above, and melted at slightly above the eutectic temperature. This heating procedure was broken into a few steps so as to rotate the sample position in the crucible to ensure homogeneity in composition.

When the reaction was complete, the sample was mounted in bakelite and prepared for microscopic examination using aluminum oxide abrasive with standard polishing methods. Micrometallographic examination and photography of the samples were carried out with bright-field illumination. The samples were etched electrolytically by alternating current.<sup>12</sup> To form an electrical circuit for etching a hole was drilled through the bakelite. A copper wire was then inserted to make contact with the sample and it was sealed with black wax. The etching solution for Ir samples was a mixture of 20% conc. HCl and 80% H<sub>2</sub>O, and that for Pt samples was the above solution saturated with NaCl. The current density for Ir samples was 15 milliamperes per mm<sup>2</sup>, and that for Pt samples was 5 milliamperes per mm<sup>2</sup>. The electric current was controlled with a Powerstat and the etching time was about two minutes.

Finally, carbon content in the sample was varied until an eutectic microstructure was obtained.

For the determination of carbon solubility in the solid, a mixture

of metal powder and graphite powder was placed in the graphite container which in turn was placed in the graphite crucible. Both were heated above the eutectic temperature, and held for a certain period of time. At the end of the heating run, the power to the furnace was shut off and the sample cooled very rapidly at a rate of about  $1000^{\circ}\text{C}$  per 5 seconds. This rapid cooling rate and the slow rate of diffusion of carbon in the metal, which are discussed in Section V, are believed to retard any solid state reaction of diffusion type. An x-ray diffraction pattern of this sample was taken using a Norelco x-ray diffraction unit with a Debye-Scherrer type camera of 11.46 cm in diameter. Nickel-filtered copper K $\alpha$  radiation was used. The lattice parameter increase due to carbon atoms was measured to obtain the solid solubility of carbon. An equation is derived in the Appendix in order to correlate the lattice parameter increase and solid solubility of an interstitial alloy.

#### IV. MATERIALS

Platinum sponge was supplied by Engelhard Industries, Inc., Newark, New Jersey. The purity given by the supplier was 99.999%, but the impurity analysis was not available.

High purity iridium sponge, 99.999% pure, was supplied by Johnson Matthey & Co., Ltd., London, England. The impurity analysis given by the supplier was:

Element:	Fe	Si	Ca	Mg	Na	Cu	Ag
Quantity:	5	5	1	1	1	<1	<1
	ppm						

Spectroscopically pure graphite rods and powder were supplied by Ultra Carbon Corp., Bay City, Michigan. The total ash content given by the supplier was about 10 ppm. The crucible made of the above rods and graphite powder were degassed at 2400°C for 2 hours in vacuum.

## V. EXPERIMENTAL RESULTS AND DISCUSSION

### 1. Platinum-Carbon Eutectic

#### Eutectic Temperature

The lowest melting temperature of Pt embedded in graphite powder was  $1705^{\circ} \pm 13^{\circ}\text{C}$ . The uncertainty of  $\pm 13^{\circ}\text{C}$  accounts for three independent errors in temperature measurement:  $\pm \sqrt{\sum x_i^2}$ . The calibration uncertainty of the pyrometer used was  $\pm 5^{\circ}\text{C}$  according to the manufacturer; and the temperature variation of the induction furnace due to fluctuating input was  $\pm 10^{\circ}\text{C}$ , and also the error in temperature readings in this temperature range was  $\pm 7^{\circ}\text{C}$ . When the sample melted, it became spherical in shape and had a bright metallic shine.

A relatively long period of time (one hour) was given to each heating run in order to ensure completion of the reaction of a sample since the rate of reaction between platinum and carbon was found to be slow, as discussed in the next section.

The reported values of the eutectic temperature by previous investigators are reasonably close to the above eutectic temperature, but still about  $25^{\circ}\text{C}$  too high. This discrepancy can be explained by either the short heating times or the chemical compositions of the samples used by previous investigators. The  $1730^{\circ} \pm 3^{\circ}\text{C}$  value reported by Collier, et al.<sup>3</sup> was determined by checking melting and freezing points of Pt in a graphite container while the temperature of their sample was made to increase or decrease. Probably the rate of temperature increase was not slow enough, resulting in a slightly elevated eutectic temperature reading; and also, obviously, their freezing point was caused by the solidification of

primary graphite flakes representing the liquidus temperature of the binary system, which were shown in their microstructure. Nadler and Kempter<sup>6</sup> employed heating times of five minutes in spite of the slow reaction rate and consequently obtained a slightly higher temperature ( $1736^{\circ} \pm 13^{\circ}\text{C}$ ) as the eutectic. On the other hand, Rudy, et al.<sup>7</sup> recorded cooling curves of Pt-C sample by means of differential thermal analysis, and took  $1732^{\circ} \pm 20^{\circ}\text{C}$  as the eutectic temperature. However, it seems that their sample was hypereutectic in composition and the temperature corresponds to the liquidus.

#### Eutectic Composition

Various carbide materials were considered as containers; but it was found that molten platinum reacted with the carbides (tungsten, tantalum, and niobium carbides) and formed an alloy with the component metal of the carbide, leaving graphite in the matrix upon cooling.<sup>13</sup> Thus, in order to determine the eutectic composition, samples of various compositions were prepared and melted on a graphite plate in a graphite crucible as described earlier. Whenever the melting temperature was too far above the eutectic, the sample stuck to the graphite plate and had to be discarded. At least a total of 10 hours heating was necessary to achieve an equilibrium microstructure. Finally, 3 equilibrium microstructures were obtained, including the eutectic (Fig. 3). The composition of this eutectic sample was 16.8 at. (1.23 wt.) %C. Fig. 4 shows a hypoeutectic microstructure with a composition of 15 at. (1.07 wt.) %C, and Fig. 5 shows a hypereutectic microstructure with a composition of 17 at. (1.25 wt.) %C. Thus, the eutectic composition of the Pt-C binary was taken as  $16.8 \pm 1.0$  at. ( $1.23 \pm 0.09$  wt.) %C. The error of

$\pm 1.0$  at. %C accounts for possible composition changes during the experiment.

The above three equilibrated samples were sent for chemical analysis to check the carbon content. The analysis of the hypoeutectic sample (15 at. %C) turned out to be 14.11 at. (1.00 wt.) %C, the eutectic (16.8 at. %C), 14.95 at. (1.07 wt.) %C, and the hypereutectic (17 at. %C) only 5.98 at. (0.39 wt.) %C. As this result was not very satisfactory, two more hypereutectic samples were prepared and sent to a different laboratory. The carbon content of both samples came out to be approximately 7 at. %. Thus, after consulting with the two laboratories, it was found that chemical analysis to check the carbon content was not very reliable since the background loss of carbon compared with the sample weight was too great.

Collier, et al.<sup>3</sup> oxidized a platinum ingot in the air at 800°C, which was previously melted in a graphite container. There was a loss of weight of 1.2 per cent (16.5 at. %C), and this loss was counted as eutectic carbon content. Even though this value comes very close to the eutectic composition determined here, the accuracy and significance are very much in doubt because it is not at all likely that the carbon in their sample got fully oxidized, and also their microstructure shows a hypereutectic structure.

#### Solubility of Carbon in Liquid Platinum

In order to determine carbon solubility in liquid platinum, pure platinum samples were melted in a graphite container, and the compositions of the samples were analysed later. The carbon content increased with time even up to 8 hours, reaching a value of 26.12 at. (2.12 wt.) %C at

1800°C. This suggested that some graphite flakes might be mechanically trapped into the liquid solution as found in the Ir-C system (Fig. 2.) This method, consequently, had to be abandoned. This experiment, however, revealed that carbon diffusion into platinum was very slow since the carbon content of a sample after 4 hours at 1800°C was only 12.35 at. (0.86 wt.) % in comparison with the eutectic composition 16.8 at. (1.23 wt.) %C at 1705°C.

#### Solid Solubility of Carbon

Solid solubility of carbon and the lattice parameter change of the metal matrix due to carbon atoms can be correlated by the equation

$$a = a_0 + a \cdot n_c \quad (1)$$

where

$$a = 2 \left[ 2\gamma_c - a_0 \left( 1 - \frac{1}{\sqrt{2}} \right) \right] \quad (4)$$

$a$  is the lattice parameter of an interstitial solid solution,  $a_0$  that of pure metal,  $n_c$  atomic fraction of carbon, and  $\gamma_c$  the radius of carbon atom. Details of the derivation of the equation are given in Appendix.

Platinum powder mixed with graphite powder was melted for 1 hour. The room temperature x-ray diffraction pattern of this sample showed fcc platinum lines and graphite lines only: no carbide lines were found. An accurate lattice parameter of this sample was obtained using the extrapolation function of J. B. Nelson and D. P. Riley.<sup>14</sup> The lattice parameter was  $a = 3.9227 \pm 0.0006 \text{ \AA}$ .

Substituting the lattice parameter of pure platinum  $a_0 = 3.9214 \pm 0.0006 \text{ \AA}$  and  $\gamma_c = 0.77 \text{ \AA}$  in Equation (4), we obtain  $a = 0.7829$ . Substituting

this value of  $a$  in Equation (1), we get:

$$\Delta a = a - a_0 = 0.7829n_c$$

Thus, the lattice parameter increase due to carbon atoms  $\Delta a = 0.0013\text{\AA}$  corresponds to 0.17 at. (0.01 wt.) %C solid solubility. If the errors in the lattice parameter are included, the maximum possible solid solubility is 0.32 at. (0.02 wt.) %C.

Thus, the Pt-C system is of a simple eutectic type with a very low solid solubility of carbon.

## 2. Iridium-Carbon Eutectic

### Eutectic Temperature

The lowest melting temperature of Ir embedded in graphite was  $2150^\circ \pm 22^\circ\text{C}$ . A relatively long heating time (2 hours) was used, considering the slow diffusion rate of carbon in this metal as pointed out by Criscione, et al.<sup>10</sup> The uncertainty of  $\pm 22^\circ\text{C}$  takes into account the calibration uncertainty of the pyrometer ( $\pm 13^\circ\text{C}$ ), the error in temperature reading ( $\pm 10^\circ\text{C}$ ), and also the inevitable temperature fluctuation of the induction furnace ( $\pm 15^\circ\text{C}$ ).

This eutectic temperature is considerably lower than the one ( $2296^\circ \pm 16^\circ\text{C}$ ) reported by Nadler and Kempster,<sup>6</sup> but this discrepancy can be explained by the fact that these investigators employed heating times of only five minutes. The value,  $2110^\circ \pm 25^\circ\text{C}$ , reported by Criscione, et al.<sup>10</sup> is in fairly good agreement. This slightly lower temperature, however, might have been due to the purity (99.7%) of their iridium. The experiment of Rudy, et al.<sup>7</sup> was apparently done with a hypereutectic sample resulting in a higher eutectic temperature.

### Eutectic Composition

Samples of various carbon contents were prepared and heated for at least 10 hours to obtain equilibrium microstructures. A 29 at. (2.49 wt.) %C sample had an eutectic microstructure as shown in Fig. 6. A 28 at. (2.35 wt.) %C sample and 30 at. (2.61 wt.) %C sample had hypo- and hypereutectic microstructure, respectively, as shown in Fig. 7 and Fig. 8. Thus, the eutectic composition was taken as  $29 \pm 1$  at. ( $2.49 \pm 0.12$  wt.) %C. When a sample was not etched, the microstructure did not reveal its fine details as can be seen in Fig. 2 compared with Fig. 6 or Fig. 7.

### Solubility of Carbon in Liquid Iridium

In order to determine the solubility of carbon in liquid iridium, it was attempted to melt pure iridium in a graphite container, but the carbon content in the liquid iridium was found to increase steadily, reaching 67.7 at. (11.6 wt.) %C after 8 hours. This value was simply much higher than the expected saturation point, and suggested that a mechanical mixing of graphite flakes was taking place. Fig. 2 shows the interaction between liquid iridium and graphite. Probably liquid iridium attacks graphite grain boundaries faster than other areas as can be seen at the left corner of the picture: a graphite flake is about to be trapped into the liquid metal. Thus, this common method of determining carbon solubility in liquid metals was not employable. The feasibility of using several refractory materials as containers was tested, but all reacted with the sample: tungsten, thoria, zirconium carbide, and tantalum carbide.

### Solid Solubility of Carbon

A mixture of iridium and graphite powder was heated at various temperatures below and above the eutectic temperature. All the room temperature x-ray diffraction patterns of this powder mixture showed only iridium and graphite lines, and no carbide lines were found. The lattice parameter of Ir melted for 1 hour in graphite, was  $3.8390 \pm 0.0006\text{\AA}$ , and that of pure iridium was  $3.8387 \pm 0.0007\text{\AA}$ . Using the same equation as in the case of the Pt-C system, we obtain  $\alpha = 0.8313$ . The lattice parameter increase  $\Delta a = 0.0003\text{\AA}$ , thus, corresponds to a carbon solid solubility of 0.04 at. (0.003 wt.) %C. If the errors are taken into account, the maximum possible solid solubility is 0.19 at. (0.01 wt.) %C.

Thus, the Ir-C system is also a simple eutectic with negligible carbon solid solubility.

## VI. CONCLUSIONS

1. The systems Pt-C and Ir-C are simple eutectics: the eutectic point of Pt-C system being  $16.8 \pm 1.0$  at. ( $1.23 \pm 0.09$  wt.) %C at  $1705^\circ \pm 13^\circ\text{C}$ , and that of Ir-C system  $29.0 \pm 1.0$  at. ( $2.49 \pm 0.12$  wt.) %C at  $2150^\circ \pm 22^\circ\text{C}$ .

2. Erroneous results were obtained by previous investigators due either to the very slow reaction rate of carbon with both metals or to samples of non-eutectic compositions.

3. The carbon solid solubility in both metals is very low.

4. Pt, with its atomic number and metallic radius greater than Ir, has lower eutectic composition and higher solid solubility of carbon than Ir, similar to the eutectics of the iron-group metals with carbon.

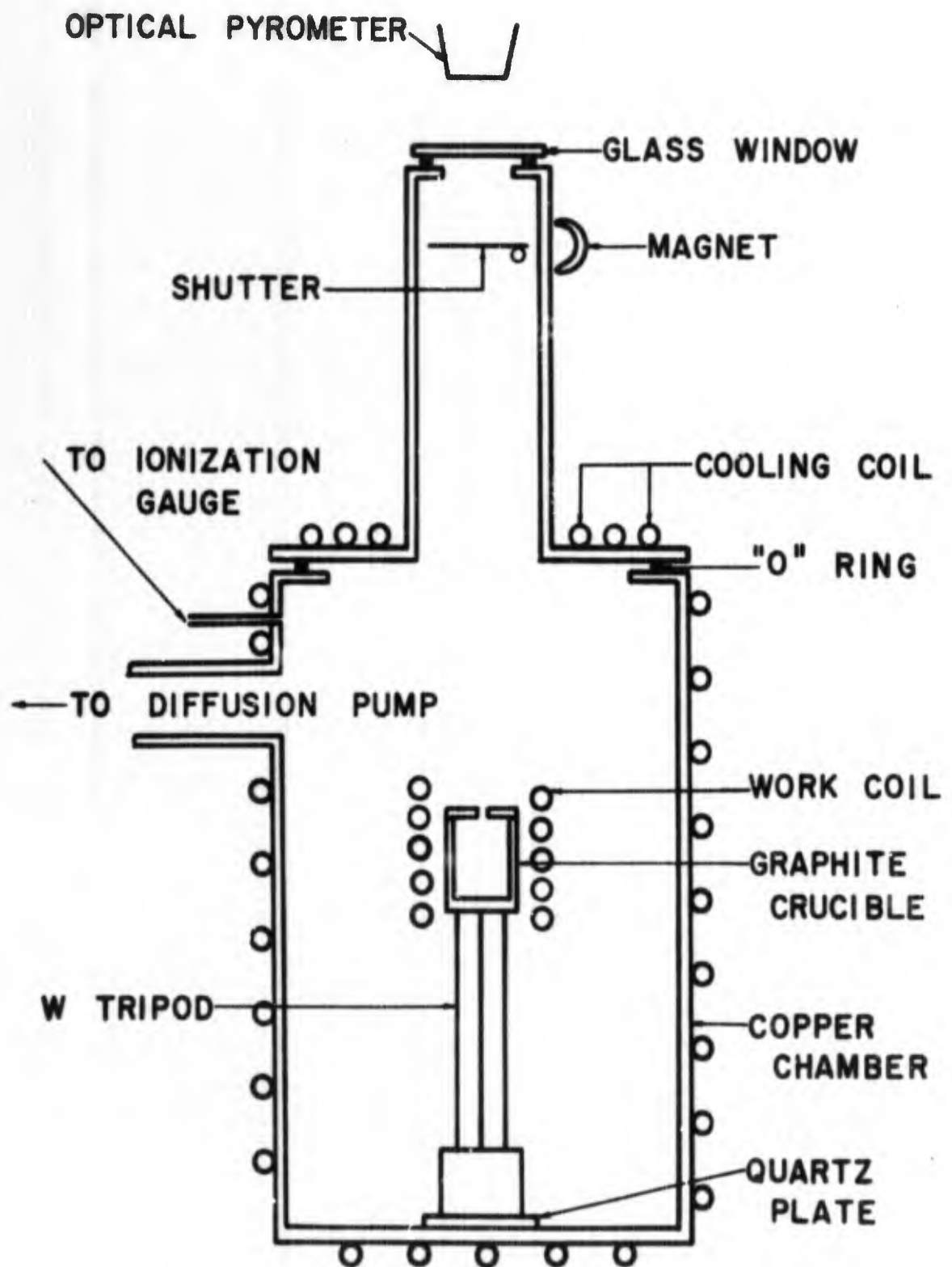
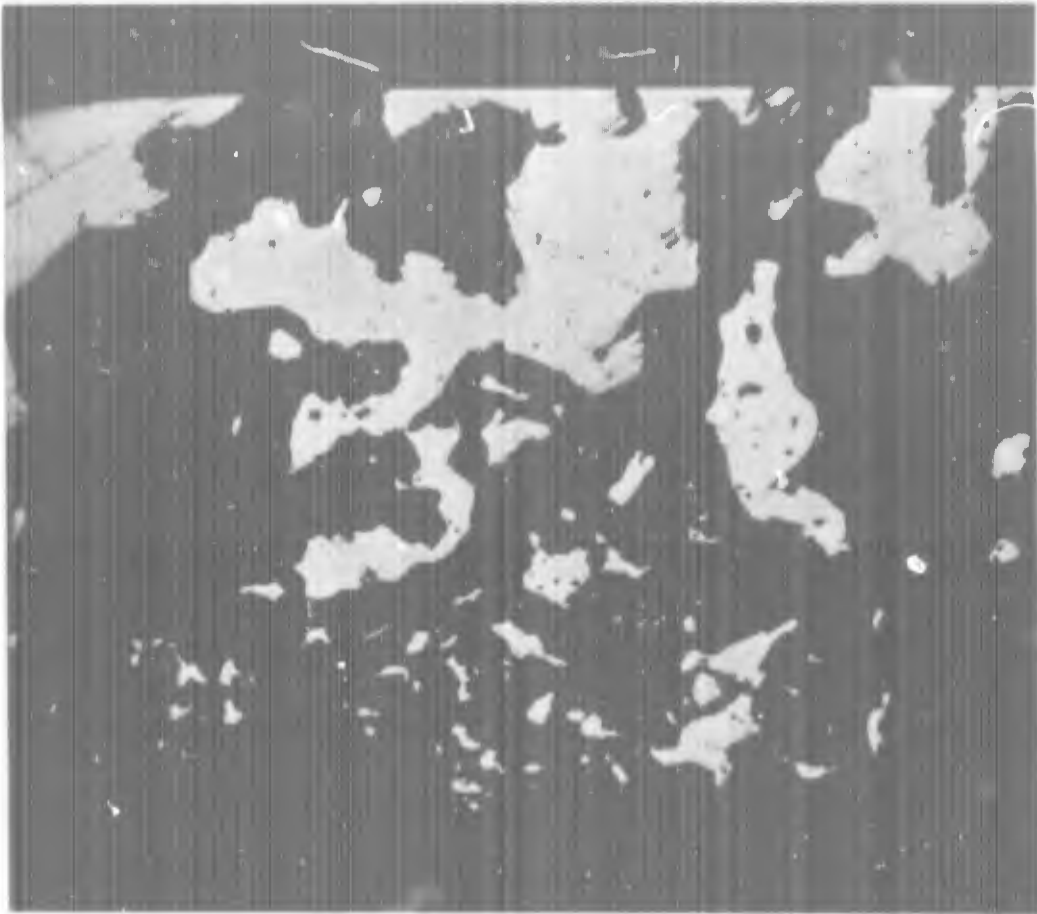
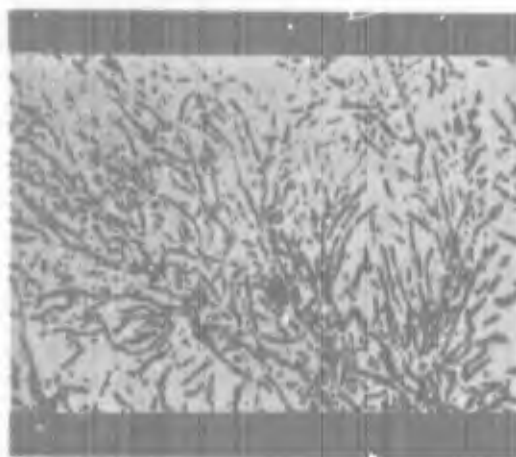


Figure 1. Vacuum Induction Furnace



**Figure 2.** Interaction between liquid iridium and graphite. Graphite flakes are being mechanically mixed into the liquid phase. 4 hours at  $2170^{\circ}\pm 25^{\circ}\text{C}$ . Unetched, X600.



X200

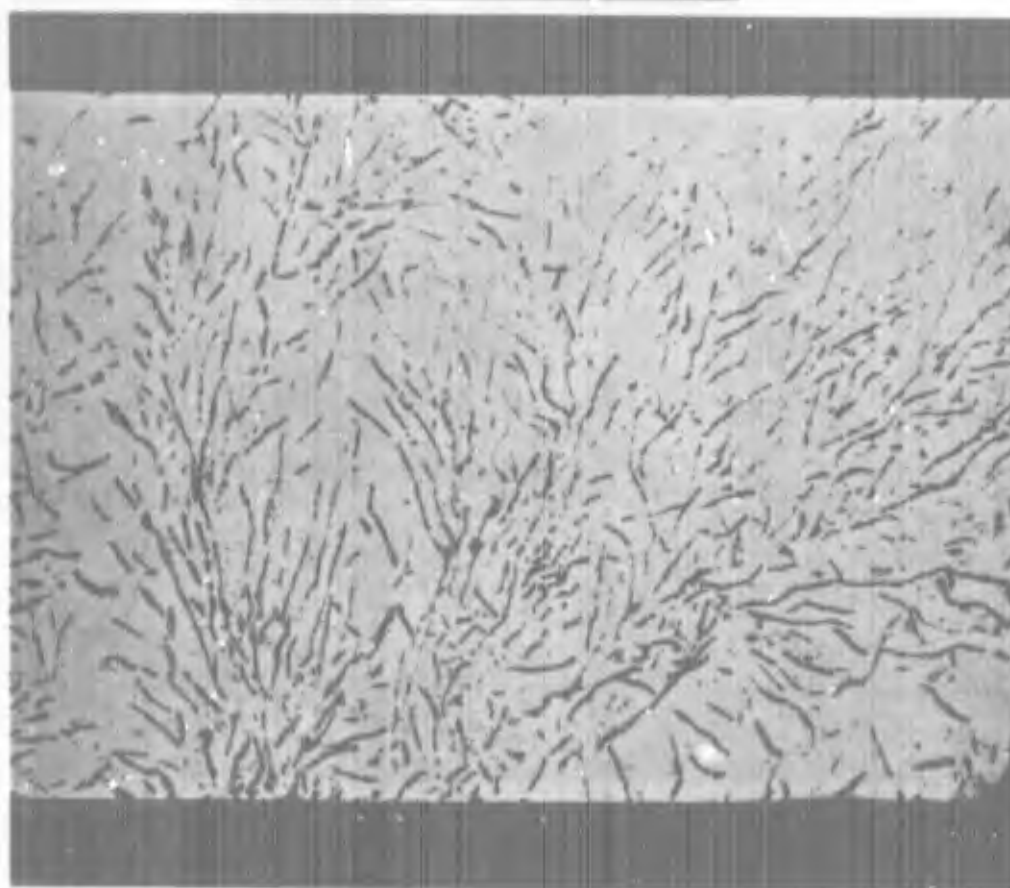


Figure 3. Eutectic Microstructure of Pt-C. 16.8 at. (1.23 wt.) %C.  $1705^{\circ} \pm 13^{\circ}\text{C}$  for 19 hours. Electrolytically etched by AC in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$  saturated with NaCl. X400

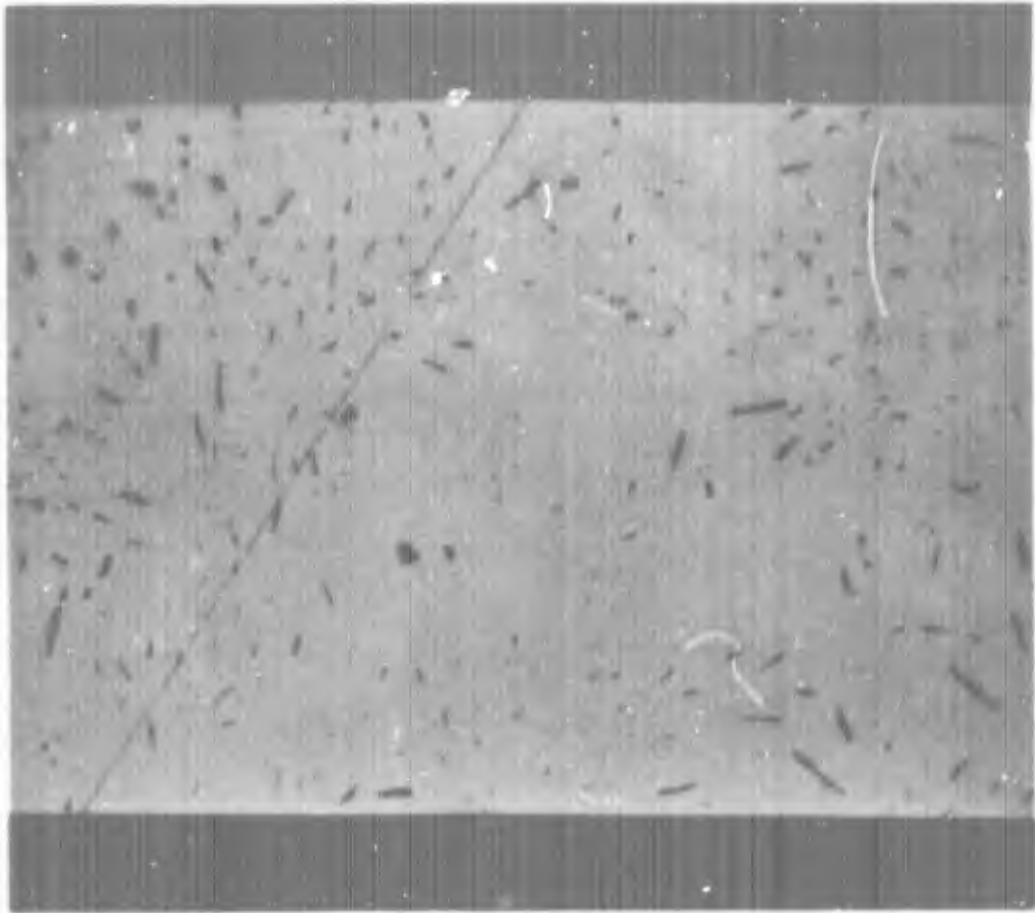


Figure 4. Hypoeutectic Microstructure of Pt-C. 15 at. (1.07 wt.) %C.  $1705^{\circ} \pm 13^{\circ}\text{C}$  for 10 hours. Electrolytically etched by AC in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$  saturated with NaCl. X200

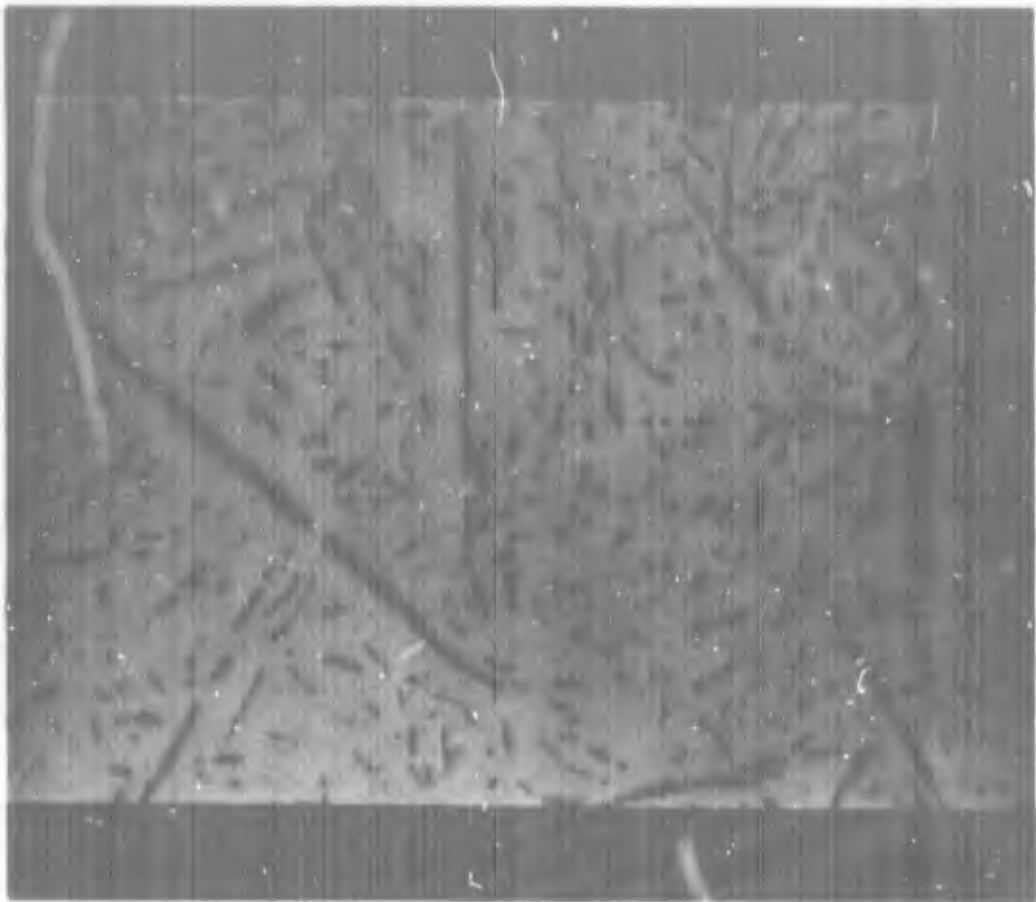


Figure 5. Hypereutectic Microstructure of Pt-C. 17 at. (1.25 wt.) %C.  $1705^{\circ} \pm 13^{\circ}\text{C}$  for 13 hours. Electrolytically etched by AC in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$  saturated with NaCl. X200

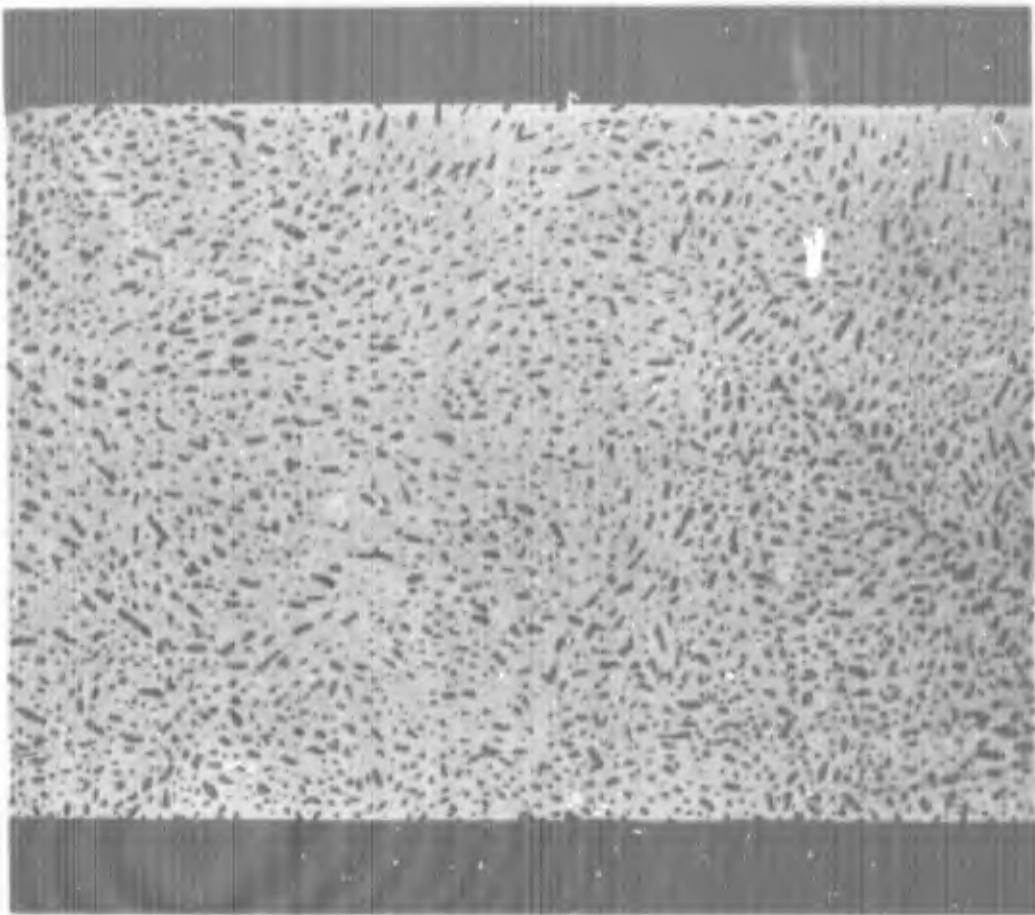


Figure 6. Eutectic Microstructure of Ir-C. 29 at. (2.49 wt.) %C.  $2150^{\circ} \pm 22^{\circ}\text{C}$  for 16 hours. Electrolytically etched in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$ . X170

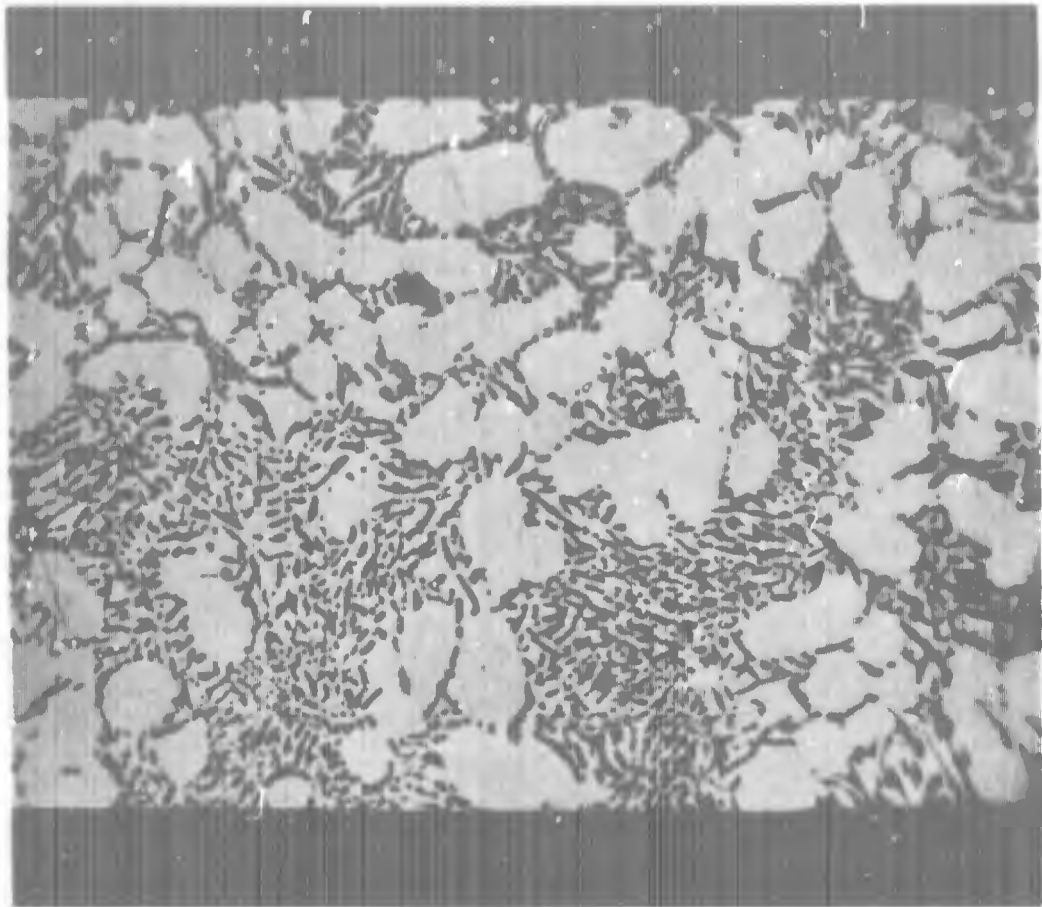


Figure 7. Hypoeutectic Microstructure of Ir-C. 28 at. (2.37 wt.) %C.  $2150^{\circ} \pm 22^{\circ}\text{C}$  for 20 hours. Electrolytically etched by AC in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$ . X450

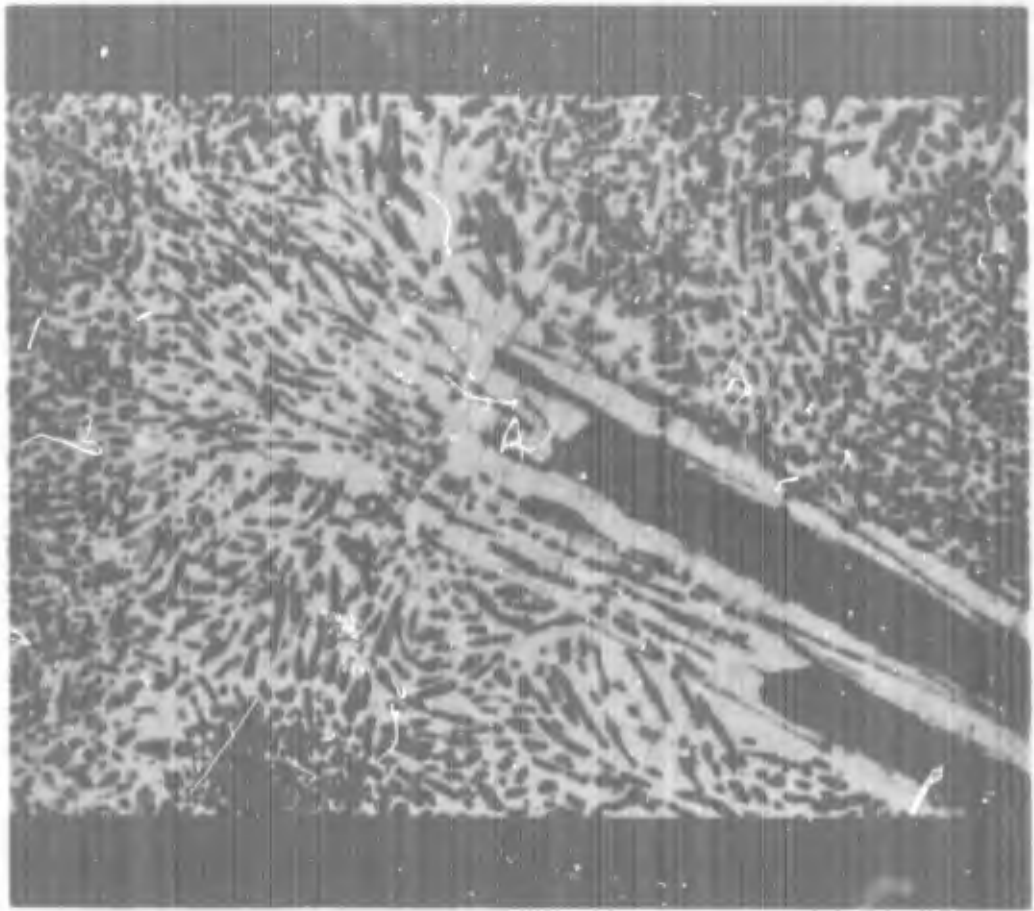


Figure 8. Hypereutectic Microstructure of Ir-C. 30 at. (2.61 wt.) %C.  $2150^{\circ} \pm 22^{\circ}\text{C}$  for 10 hours. Electrolytically etched by AC in a solution of 20% conc. HCl and 80%  $\text{H}_2\text{O}$ . X400

## VII. APPENDIX

The following expression for the lattice expansion due to interstitial atoms is valid at a low concentration of solute:

$$a = a_0 + \alpha \cdot n_c \quad (1)$$

where  $a$  is the lattice parameter of an interstitial solid solution in Å unit,  $a_0$  that of pure metal,  $\alpha$  a constant in a particular system, and  $n_c$  atomic fraction of interstitial atoms, in this case, carbon atoms. In case of an fcc metal, if all the octahedral voids are filled with interstitial atoms, the resulting structure will be a NaCl type (see Fig. 9). If a hard sphere model is employed for this lattice, the final lattice parameter with  $n_c = 0.5$  will be:

$$a = 2(\gamma_m + \gamma_c) \quad (2)$$

where  $\gamma_m$  is the radius of metal atoms, and  $\gamma_c$  is that of carbon atom. The value of  $\gamma_m$  is obtained from the lattice parameter of the pure fcc metal:

$$\gamma_m = \frac{a_0}{2\sqrt{2}}$$

Substituting this in Eq. (2), we get

$$a = \frac{a_0}{\sqrt{2}} + 2\gamma_c \quad (3)$$

When all the octahedral voids are filled, that is,  $n_c = 0.5$ , Eq. (1) is equal to Eq. (3):

$$a_0 + a \cdot 0.5 = \frac{a_0}{\sqrt{2}} + 2\gamma_c$$

$$a = 2\left[2\gamma_c - a_0\left(1 - \frac{1}{\sqrt{2}}\right)\right] \quad (4)$$

Now, if we know of  $\gamma_c$  and  $a_0$ , the coefficient of lattice expansion due to interstitial atoms can be calculated.

If we take  $\gamma_c = 0.77\text{\AA}$  of diamond, in case of  $\gamma$ -Fe, we get  $a = 0.9974$ . With this  $a$  value, the calculated lattice parameter change of  $\gamma$ -Fe due to carbon atoms agrees very well with the experimental data.<sup>15</sup> For example; at  $n_c = 0.001$ , the calculated value,  $\Delta a_{\text{cal}} = 0.0010\text{\AA}$  is equal to the experimentally observed value  $\Delta a_{\text{exp}} = 0.0010\text{\AA}$ .  $\Delta a$  is the lattice parameter increase due to the presence of carbon.

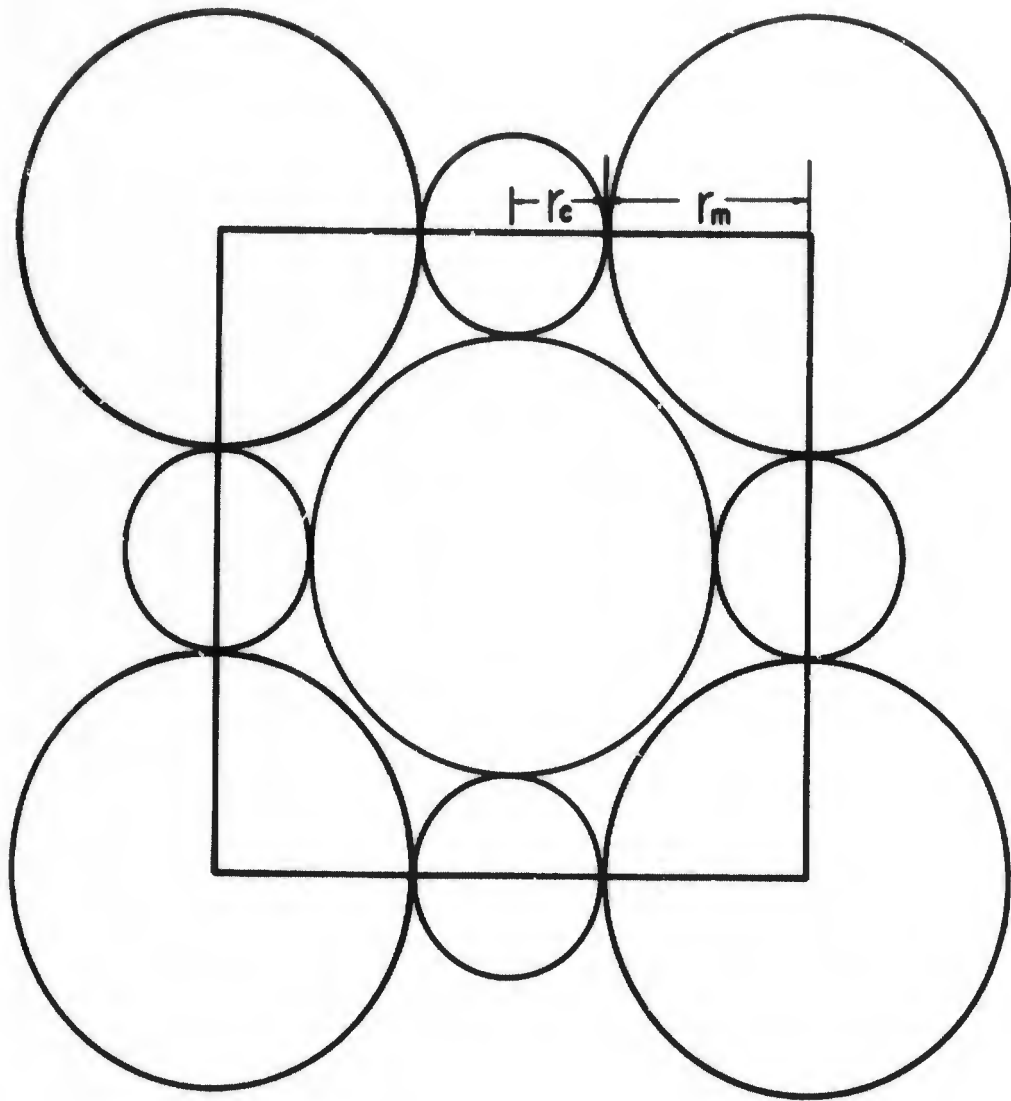


Figure 9. (100) Plane of NaCl Type Structure

## VIII. REFERENCES

1. M. Hansen, Constitution of Binary Alloys, McGraw-Hill Book Co., Inc., New York (1958).
2. C. S. Barrett, Structure of Metals, McGraw-Hill Book Co., Inc., New York, 646-647 (1952).
3. L. J. Collier, T. H. Harrison, and W. G. A. Taylor, *Trans. Faraday Soc.* 30, 581-587 (1934).
4. Johnson, Matthey & Co., Ltd., *Platinum Metals Review* 8, 101 (1964).
5. E. Raub and G. Falkenburg, *Z. Metallkunde* 55, 186-189 (1964).
6. M. R. Nadler and C. P. Kempter, *J. Phys. Chem.* 64, 1468 (1960).
7. E. Rudy, D. P. Harmon, Sacramento Plant, Aerojet-General Corp. First Progress Report on Iridium Base Alloys and Their Behavior in the Presence of Carbon, Contract AF 33(615)-2668, (Sept. 1965).
8. D. R. Lovejoy, *Can. J. Phys.* 36 [7], 1397-1408 (1958).
9. A. A. Hasapis, A. J. Melveger, M. B. Panish, L. Reif, C. L. Rosen, WADD-TR-60-463, Pt. II 4 (1964).
10. J. M. Criscione, R. A. Mercuri, E. P. Schram, A. W. Smith, H. F. Volk, ML-TDR-64-173, Pt. II 70 (Jan. 1965).
11. H. S. Stimson, *J. Res. Nat. Bur. Std. A.* 65, 139 (1961).
12. G. L. Kehl, The Principles of Metallographic Laboratory Practice, McGraw-Hill Book Co., Inc., New York, 433-434 (1949).
13. E. Raub, G. Falkenburg, *Z. Metallkunde* 55, 190-192 (1964).
14. L. V. Azaroff, M. J. Buerger, The Powder Method in X-Ray Crystallography, McGraw-Hill Book Co., Inc., New York, 238 (1958).
15. W. P. Pearson, Handbook of Lattice Spacings and Structures of Metals, Pergamon Press, London, 920 (1958).

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DOCUMENT CONTROL DATA - R&D		
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1. ORIGINATING ACTIVITY (Corporate author) Materials Science Program University of Cincinnati Cincinnati, Ohio 45221		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP N.A.
3. REPORT TITLE The Systems Platinum-Carbon and Iridium-Carbon		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report 1 September 1963 - 31 August 1965		
5. AUTHOR(S) (Last name, first name, initial) Hoch, M. and Rhee, S. K.		
6. REPORT DATE June 1966	7a. TOTAL NO. OF PAGES 29	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. AF 33(657)-9048	9a. ORIGINATOR'S REPORT NUMBER(S) AFML TR 66-181	
b. PROJECT NO.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) None	
c.		
d.		
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13. ABSTRACT The eutectics in the Pt-C and Ir-C phase diagrams were studied in this investigation. Both systems are of a simple eutectic type with very limited solid solubility of carbon. The eutectic point of the Pt-C systems exists at $16.8 \pm 1.0$ at. ( $1.23 \pm 0.09$ wt.) %C and $1705^\circ \pm 13^\circ\text{C}$ , and that of the Ir-C system at $29.0 \pm 1.0$ at. ( $2.49 \pm 1.0$ at. ( $2.49 \pm 0.12$ wt.) %C and $2150^\circ \pm 22^\circ\text{C}$ , respectively.		

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