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Copper Chromium Alloys And Emulsions.



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COPPER CHROMIUM ALLOYS AND EMULSIONS

BY

TERRENCE ONAS WESTHAFFER  
B. A. University of Oklahoma, 1914

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1916



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June 1 1916

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-  
VISION BY Terrence Onas Westhafer

ENTITLED Copper Chromium Alloys and Emulsions

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE  
DEGREE OF Master of Science

D. F. McFarland

In Charge of Thesis

W. A. Noyes

Head of Department

Recommendation concurred in:\*

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\_\_\_\_\_  
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} Committee  
on  
Final Examination\*

\*Required for doctor's degree but not for master's.

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COPPER CHROMIUM ALLOYS AND EMULSIONS

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I. Introduction.

1. The Purpose of the Investigation.

The purpose of this investigation has been three-fold, (1) to determine the limits of the mutual solubility of chromium and copper, both in the liquid and in the solid state, (2) to ascertain whether the metals form solid solutions at some ranges of concentration, and (3) to establish the presence or absence of eutectics in the series.

2. The present Status of the Field.

The data published previous to the more recent years are meager and conflicting. The earlier workers were concerned with methods of making the alloys of copper and chromium, and with the solubility of chromium in copper and of copper in chromium in the mixtures obtained by their several methods.

H. Moissan<sup>1</sup> prepared a mixture of the two metals in which about .5% chromium dissolved in copper. Jassoneix<sup>2</sup> placed the solubility of chromium in boiling copper at 1.6%. Hamilton and Smith,<sup>3</sup> by reducing Cr<sub>2</sub>O<sub>3</sub> with carbon in the presence of molten copper, succeeded in preparing alloys of a gray-red color, containing quite appreciable amounts of impurities. A typical analysis

<sup>1</sup> H. Moissan, Compt. Rend. 119 (1894) p. 185; 122 (1896)p.1302

<sup>2</sup> Binet de Jassoneix, Compt. Rend. 144 (1907) p. 915.

<sup>3</sup> Hamilton and Smith, J. Am. Chem. Soc. 23 (1901) p. 151.



of an alloy made by this method follows:

Copper	88.18%
Chromium	3.22
Iron	1.35
Carbon	2.38
Gangue	4.13

They report a maximum solubility of chromium in copper of over seven percent.

It remained for Hindrichs<sup>4</sup> in 1908 to attempt a more systematic study of the system in connection with a series of investigations on the alloys of both chromium and manganese with various metals, including copper and silver. In spite of the extraordinary difficulties which attended the research, due mainly to the chemical perversity of the constituent chromium, he succeeded in establishing several points on the thermal equilibrium diagram. He left undecided the question whether at some range of concentration the metals do not form solutions in the solid state. Neither did the data obtained warrant a statement as to the course of the solubility curve of the molten metals. In fact, the upper portion of the thermal curve can only be guessed at. As a result of the microscopical study of the alloys he obtained, Hindrichs determined that above the melting point of both metals emulsions are formed in which, on cooling, first the drops of chromium and then the drops of copper crystallise out. This, of course, would account for the apparent greater solubility of chromium in copper reported by previous workers. His research definitely established the system as one in which the metals are only partially immiscible between certain concentration and temperature ranges. It is also quite evident that copper dissolved in

<sup>4</sup> G. Hindrichs, Z. anorg. allgem. Chem. 59 (1908) p. 414.





chromium lowers its melting point from 1553<sup>o</sup> C. to 1468<sup>o</sup> C., and that less than .5% chromium dissolved in copper produces the maximum lowering of its melting point from 1083<sup>o</sup> C. to 1076<sup>o</sup> C. Altho his microscopical study gave no evidence of a eutectic, a consideration of the thermal data leads to the probability of its existence at a concentration of chromium of less than .5%. Hindrichs reported no analysis of the alloys prepared.

Recently McFarland and Harder<sup>5</sup> noted that the highest chromium content obtained in alloys of chromium and copper was 13.15%, and in all mixtures of the series containing more than 6% of chromium there occurred on cooling a marked separation of chromium or a chromium rich constituent. By cooling a melt of equal proportions very slowly, they succeeded in obtaining in the solid state a well defined separation, one layer consisting of chromium containing some copper, and the other of copper containing some chromium.

Still more recently Sebast and Gray<sup>6</sup> have found that the addition of pure chromium to copper increases the resistivity of the copper only very slightly. This seems to indicate that chromium is only very slightly soluble in copper in the solid state.

### 3. The Outline of the present Investigation.

(1) A type of gas furnace has been evolved which gives a fairly adequate temperature range for the melting of the mixtures.

(2) Cooling curves have been taken of mixtures of copper and chromium up to equal percentages of each. Mixtures of higher

<sup>5</sup>McFarland and Harder, Trans. Am. Inst. Met. 9 (1915).

<sup>c</sup>Sebast and Gray, Advance Copy 19, 29th Genl. Mtg. Am. El.-ch.S.



chromium content presented such insurmountable difficulties that their thermal study was abandoned.

(3) A series of alloys of copper and chromium of low chromium content has been prepared. The microstructure of specimens from this series has been studied and photographed.

(4) The alloys of this series have been analysed.

## II. Experimental.

### 1. The General Method of Attack.

From the first it seemed that the proper method to attack the problem in hand, in regard both to the constitutional diagram and the microstructure, would be one which would allow the two metals to be melted together and held at a high temperature until the system could arrive at equilibrium. In Hindrichs' work, which has been mentioned previously, the marked chemical action of the chromium on the materials it touched and with the oxygen of the air made it necessary for small masses to be melted up and cooling curves to be taken as quickly as possible. The average rate of cooling in his determinations approached  $20^{\circ}$  to  $30^{\circ}$  in ten seconds. Such a rapid rate of cooling might well be the cause of a failure of the recording instrument to show the slight heat effect of the crystallization of small amounts of chromium, since chromium has a strong tendency to become viscous at temperatures not far above its freezing point. It is also probable that the system could not have come to complete equilibrium in the short time in which the melt was held above the temperature at which both metals are entirely liquid, and diffuse readily. It is quite probable, therefore, that such a method was



not conducive to obtaining accurate results from the standpoint of determining the arrest points in cooling or of producing microstructures representative of the melts of the compositions finally obtained. Hence, it was proposed to develop a method and apparatus which would avoid such a possibility.

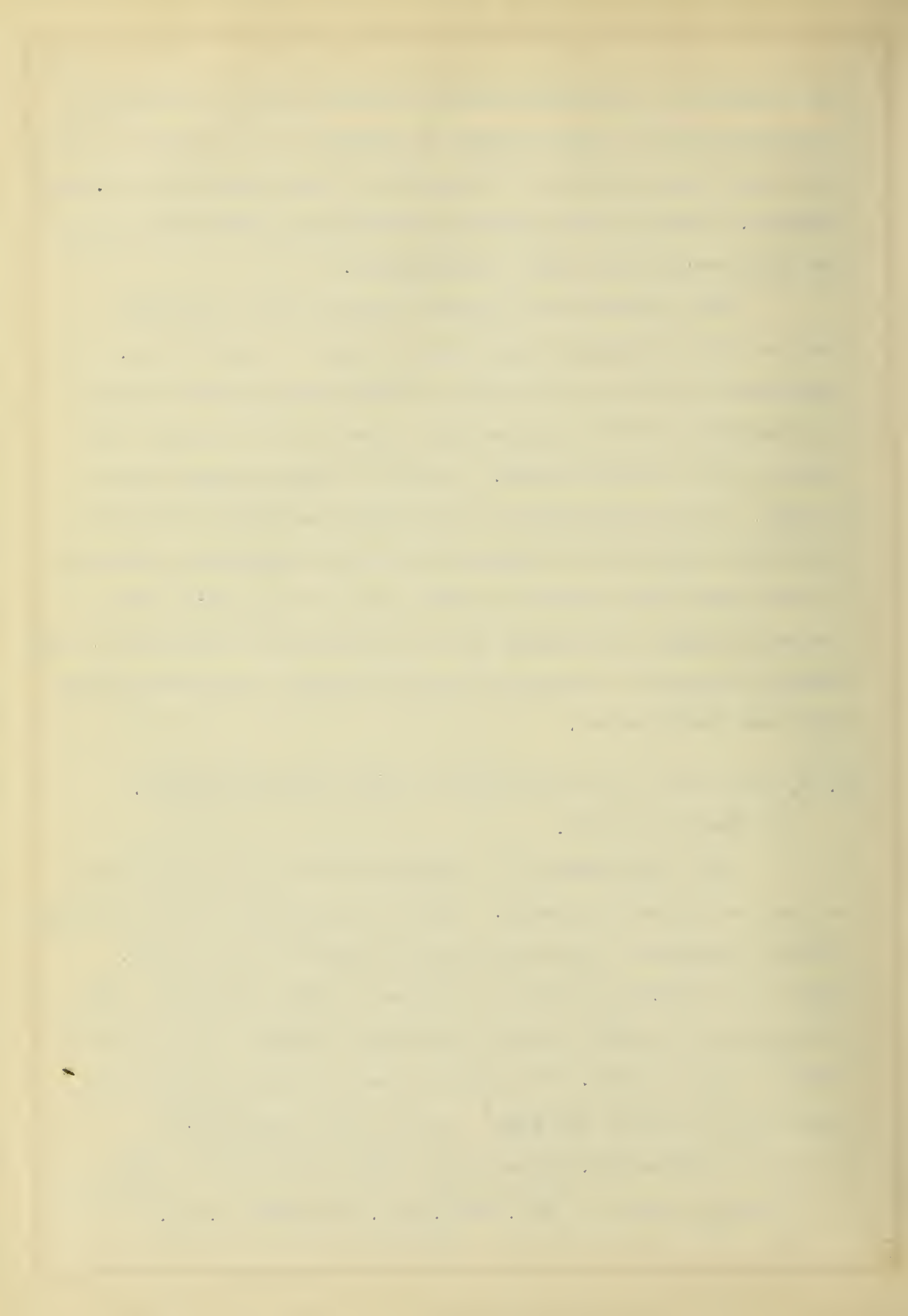
Such a method would demand, first of all, adequate time for the thoroughly liquid melt to come to equilibrium. A sufficiently slow rate of cooling should be employed to insure the recording of the slightest heat effect at the instant any change in the system occurred. A melt of larger weight should be used. To accomplish this would require materials (1) sufficiently refractory to withstand the high temperature necessary for the time during which the metals were being melted, held for equilibrium, and cooled, and (2) sufficiently resistant to the chemical action of chromium and slags employed, wherever contact with them should occur.

## 2. The Apparatus and Methods used in the Thermal Analysis.

### (1) Furnaces tried.

The development of a furnace suitable for the problem in hand was first considered. There is available in the laboratory electric connection furnishing thirty amperes at 110 volts. Harder, in connection with his studies in this laboratory, had developed an electric granular resistance furnace, which it was thought could be used. This furnace was a modification of one described by Calhane and Bard<sup>6</sup>, and is fully described in the above reference (3). It consisted essentially of an outer

<sup>6</sup> Calhane and Bard, Met. Chem. Eng. 10 (1912) p.461.



shell of fireclay, supported on a circular base of the same material. Within the outer cylinder was a smaller, tight fitting cylinder of pure fused magnesia. The crucibles for holding the melt, and the crucible supports were made of the same material. Electrodes of graphite were employed. The resistor, a mixture of graphite and compressed carbon, in small enough particles to pass a ten mesh and lie on a twenty mesh sieve, had a total cross-sectional area of 2 to 2.25 square inches. An outer resistance was provided to be used as the current rose.

Considerable time was expended in an effort to regulate the furnace so that it would be suitable for the determination of cooling curves. It was comparatively easy to melt chromium with the resistor recommended by Harder; i.e. a mixture of graphite and compressed carbon. The first difficulty which presented itself, and one which was never overcome, was that of arcing and resulting unequal heating within the resistor. Various compositions of the resistor were tried from pure graphite to pure compressed carbon, at sizes of the individual grains varying from larger than ten mesh to smaller than twenty. Various pressures on the resistor and methods of increasing or decreasing steadily and uniformly this pressure suggested themselves. In spite of all efforts to maintain a uniform composition and pressure in the resistor, arcing would ultimately set in at high temperatures, with the result that the crucible and melt were unequally heated, and the parts immediately in contact with the arcs would fuse. Such a condition was, of course, not promising for adequate cooling curve determination; and since the difficulty could not be overcome, the scheme was finally abandoned.





The idea then suggested itself that the melts be made in the large Hoskins Carbon Plate resistance furnace available in this laboratory. If the melts could be held for a sufficient length of time to insure equilibrium, some means could be provided by which each melt could be transferred quickly to a preheated cooling furnace, and the cooling curve subsequently registered.

(2) Crucibles developed.

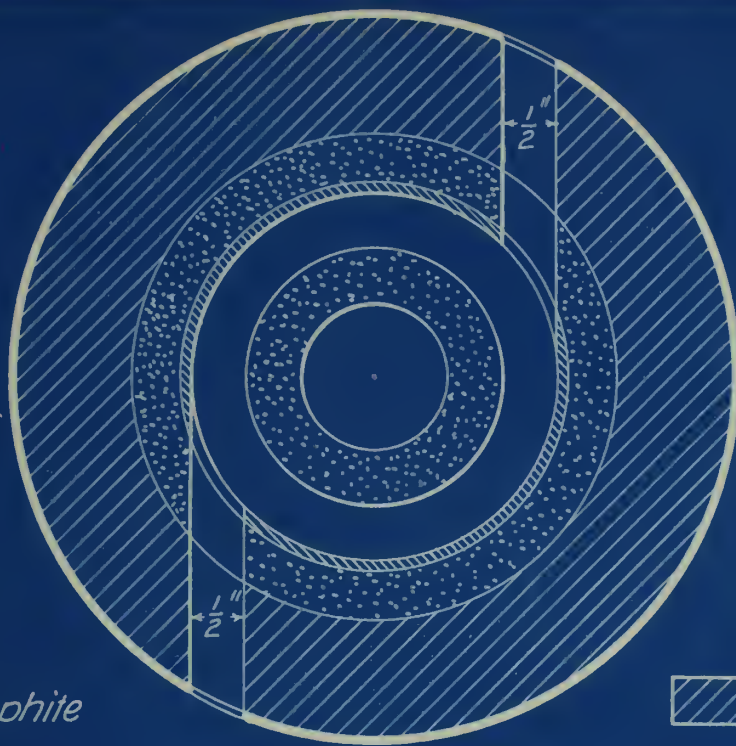
The problem then became one of developing a crucible that would withstand the high temperature of the furnace a suitable length of time, and then possess great enough tenacity to permit it to be transferred by some specially designed appliance from the heating furnace to the cooling furnace. The material of such a crucible must of course be quite resistant to the action of chromium at the high temperatures employed. The prevailing scarcity and high price of magnesia for making magnesia crucibles by the method used by Yensen<sup>9</sup> in melting electrolytic iron was at this time the governing factor in preventing a trial of such crucibles. Then, too, it had been noted by Hindrichs that crucibles of magnesia were somewhat acted upon by molten chromium, and it was quite evident that magnesia would demand the use of a basic slag as a cover for the melt.

At this time zirconia was brought to our attention as a material which was fairly cheap and at the same time possessed the very desirable properties of being very refractory and neutral in chemical action. Consequently, some powdered zirconia, containing 38% zirconium oxide, was secured from the Foote Mineral Company, and a series of tests was made with it.

For the purpose of making the crucible from this raw

<sup>9</sup> Yensen, Bull. No. 72, Eng. Exp. Sta., U. of Ill., (1914) p. 49.





Graphite



Silica



Alundun cement



Fireclay

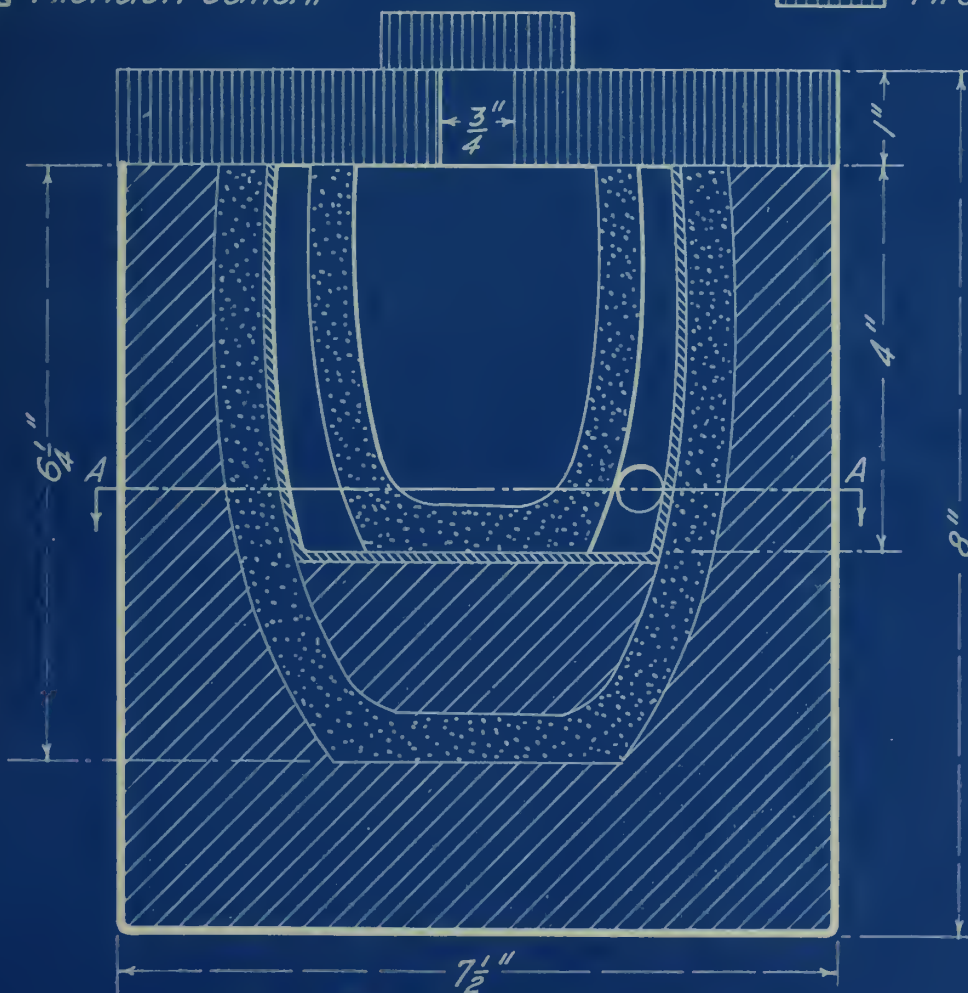


Fig 1 Gas Furnace



material a suitable mold was developed. A picture of this mold is to be seen in Fig. 2., and a full size drawing in Fig. 3. The mold was machined from steel. The neck of the plunger was made of the proper dimensions to fit into a press giving a pressure of about six thousand pounds. This press was made available through the courtesy of the Ceramics Department of the University.

Three types of binders were tried out; magnesia, alumina, and gum tragacanth. Several crucibles were molded with the use of each type of binder in different proportions. A number of crucibles were also prepared with no binding material whatever. With a little manipulating of the amount of binder and water in the mix, good results were obtained with all these methods and a sufficient number of flawless crucibles was molded and preserved for tests.

These crucibles were dried thoroughly at room temperature then heated further at  $100^{\circ}\text{C}$ . for periods varying from twelve to forty-eight hours. They were then placed in the Hoskins furnace and heated up slowly to the temperature needed for the investigation. In no case did a single crucible withstand the action of the intense heat. In fact, a white heat was in general sufficient to cause the collapse of the crucible.

The use of pure zirconium oxide was prevented because of its high price.

These results led to a reconsideration of the silica-lined graphite crucible, which has been used with much success by Professor Parr of this laboratory, and by Harder in connection with the investigation already mentioned. This crucible had



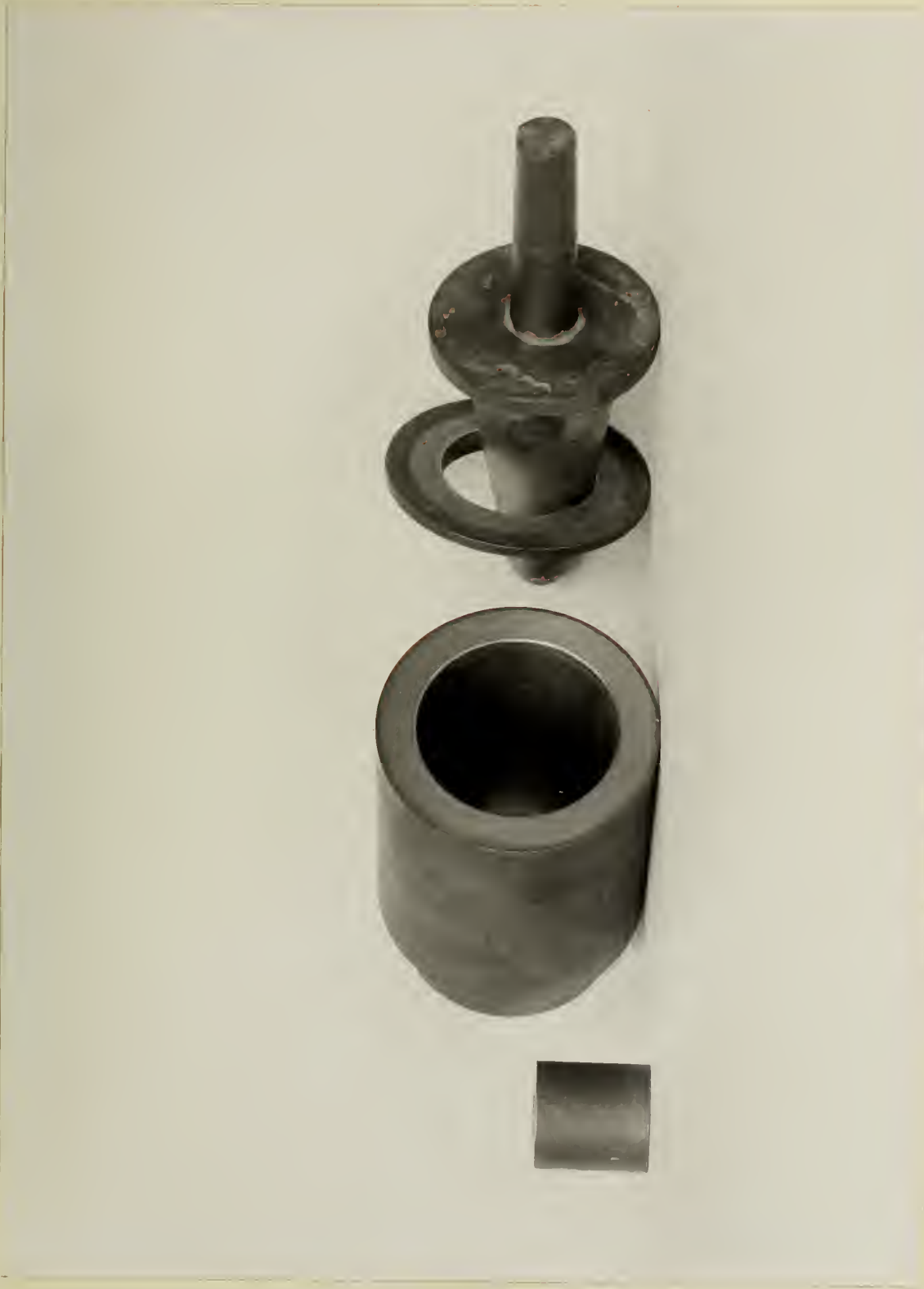


Fig. 2. Steel Crucible Mold





the advantage of being readily obtainable at a fair cost, but it had exhibited the disadvantage of insufficient refractory properties when exceedingly high temperatures were used in the Hoskins furnace.

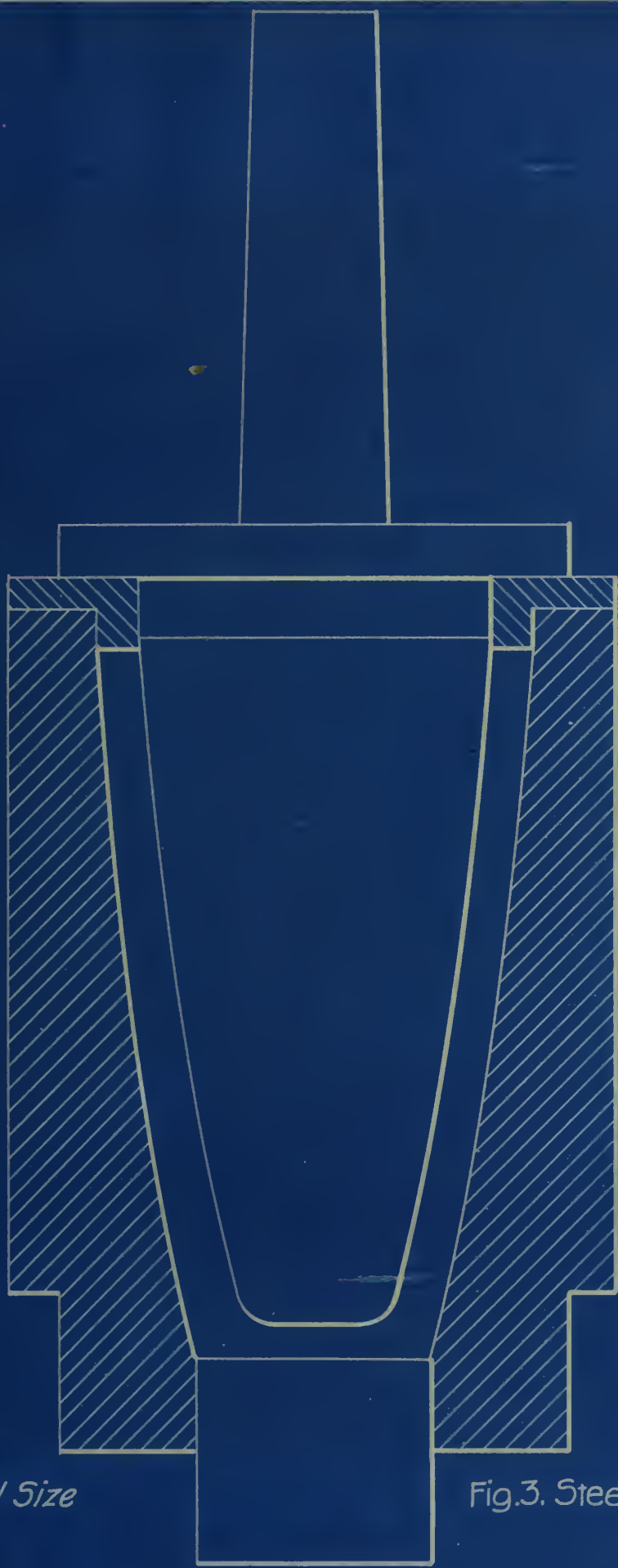
Even with the use of the silica lined graphite crucible the idea of making the melts in the large furnace and transferring them to a smaller cooling furnace had to be abandoned. The time required for the transfer and the proper adjusting of the apparatus could not be shortened sufficiently to allow the introduction of the pyrometer tube at the necessary moment. The attendant difficulties of such a transfer in the presence of such extreme heat made it impossible to continue with the plan.

### (3) Gas Furnace finally used.

It was suggested at this point that probably a gas furnace could be devised, which could at once be used for a heating furnace and a cooling chamber. Acting on this suggestion, a furnace of the type shown in Fig. 1 was finally evolved. This furnace was of very simple construction. The form which gave the best results consisted of an outer container of sheet iron. Within this was a No. 9 Dixon graphite crucible. The space between was tightly packed with powdered silica. The crucible was brasqued with a thin coating of alundum cement, and enough space was left to accommodate a No 3. graphite crucible sitting within. Holes leading in from opposite sides at the base of the firebox admitted the blast burners used for heating.

The advantages of this construction are evident. First, the spiral motion of the blast flame within the heating chamber allowed the longest possible time of contact of the flame with





*Full Size*

Fig.3. Steel Crucible Mold



the crucible holding the melt. Secondly, the blast escaped from under the edge of the crucible lid, and was prevented from acting on the surface of the melt by the close fitting furnace lid. Thirdly, the simplicity of construction allowed the furnace to be rebuilt, when burned out, with the minimum time and effort.

The disadvantages for the purpose in hand are also obvious. Although the furnace possessed a rate of cooling which was fairly constant and of the proper magnitude, the factors involved could evidently never be exactly the same at all times. Then, too, the speed with which the highest temperature could be attained depended upon the gas pressure available. Consequently, the most propitious times to make runs had to be sought, when the minimum use was being made of the gas at other places in the laboratory. Finally, the strong atmosphere of oxygen in excess of the gas used made doubly necessary the use of an adequate cover for the melt.

#### (4) Cover Substances for Melts.

Attention was next directed to the use of the cover needed. Hindrichs did not succeed in preventing the oxidation of chromium by the use of a neutral gaseous atmosphere. To avoid such a contingency, and for reasons mentioned already, a cover substance was sought which would have a melting point below that of copper and a boiling or sublimation point above the maximum temperature to be used. It was required in addition that the cover substance should degasify the melt, without excessive reaction with the chromium or with the tube used for the protection of the thermocouple.



The consideration of this factor demanded a simultaneous study of suitable protecting tubes and cover slags. The protecting tubes in common use are quartz, porcelain, and alundum. These were tried out successively in mixtures of the two metals and in different cover substances alone. The use of quartz tubes precluded the use of cryolite, which has proven such a valuable cover heretofore. Neither could porcelain be used with such a slag. Cryolite also had the disadvantage of being quite volatile at temperatures above  $1300^{\circ}\text{C}$ . Borax glass alone was without effect on any of the tubes, but with a chromium melt it exhibited a very decided tendency to react with the chromium, and at the surface of contact with the melt etched the quartz and porcelain tubes badly. It had the further disadvantage of becoming viscous on reaction with chromium or its oxide, and including mechanically small particles of chromium. Calcium fluoride, with or without chromium, etched all tubes. Boric acid was open to the same objection as borax. Salt and a mixture of sodium and potassium chlorides were too volatile to be used even at the lower temperatures. Various other combinations of these and other substances with silica were tried without as much success as attended the same substances when tried alone. Three Stonax tubes, obtained from the Norton Company, were either broken the instant of touching the melt or badly acted upon by the slag and chromium. These results led finally to the use of quartz tubes and carbon covers for melts of lower chromium content, and graphite tubes for those of higher chromium content.

This introduced another factor that demanded attention. Chromium was melted in a graphite crucible and analysed by the





combustion method for carbon. The analysis showed a very slight percentage of carbon, which must have been due chiefly to mechanically included carbon. Microscopical analysis did not show that chromium so melted differed in structure from pure chromium, with the exception of spots of carbon mechanically included. It appeared quite probable therefore, that although Moissan<sup>10</sup> had succeeded in making two carbides of chromium at the temperature of the electric arc, the reaction must have been exceedingly slow in the region of 1600°C. For the purpose in hand, therefore, it was decided to make use not only of carbon or graphite particles for covering the melt, but also of a graphite crucible for containing it.

(5) The Temperature indicating Instrument.

The reading of temperatures was accomplished by the use of a Leeds and Northrup Potentiometer Indicator (No. 10774) and a platinum and platinum-rhodium thermo-couple. The instrument read directly in degrees centigrade. A device for correcting for the temperature of the cold junction obviated the necessity of using the zero junction. The instrument could be read within two degrees.

(6) Method of reading Fall in Temperature of Cooling Melt.

The method of taking the cooling curve readings was greatly simplified by the use of this apparatus. The furnace was started with crucible in place, and the proper amount of copper for a three hundred gram melt was poured into the crucible through a hole in the furnace lid. A few pieces of graphite on top of the copper were sufficient to prevent oxidation. The potentiometer was set up at a convenient distance from the furnace. At about

<sup>10</sup>H. Moissan, Le Four Electrique, p. 206.



the melting point of chromium, the proper amount of chromium was added, and graphite particles thrown in thereafter as needed. After the mixture was thoroughly molten, the temperature was maintained at periods varying from one to two hours with frequent stirring. The quartz protecting tube was then introduced with the couple, the gas and air shut off, the instrument adjusted, and readings taken at intervals of one-half to one minute. About one and one-half inches of the quartz protecting tube were destroyed on the cooling of each melt. The tube was then fused with the oxy-acetylene flame and used again.

Previous to taking the cooling curves herein reported, the couple and apparatus were carefully calibrated by the use as fixed points of the melting point of copper under reducing atmosphere,  $1084^{\circ}\text{C}$ ., and the boiling point of sulphur under standard conditions,  $447.7^{\circ}$ . A series of four careful determinations at the outset with each fixed point yielded the average values of  $1083^{\circ}\text{C}$ . and  $447^{\circ}\text{C}$ . respectively. Considering the accuracy with which the instrument could be read these were quite satisfactory. The data are not reported herein.

The method was varied somewhat in the case of the cooling curve for the melt of fifty percent chromium. Here a graphite tube five-eighths of an inch in diameter outside, and three-eighths of an inch inside diameter was used. The pyrometer couple was prevented from touching the graphite by the use of a two-hole alundum tube. The tube was hollowed out by means of a knife point deep enough so that the end of the couple could be completely shielded from the graphite.



### 3. The Apparatus and Method used in Preparing Alloys for Microscopic Examination.

#### (1) Furnace used.

A different type of furnace was used later in the investigation. A thick fireclay cylinder was substituted for the sheet iron container in the hope that less radiation would follow. An air preheater, consisting of an iron pipe passing through a common gas combustion furnace, was used. The furnace was heated by one burner only, which was considerably larger than the burners used with the first furnace. This furnace was readily repaired and gave good service.

#### (2) Method of Melting and Casting.

The melts were made in the same manner as before, with the exception that the furnace was heated to quite a high temperature before the introduction of the melt.

After the mixture had been subjected to the maximum temperature of the furnace for two hours, the melt was lifted and poured into two iron molds embedded in powdered silica. These were previously lined with best quality asbestos paper, and preheated to red heat to drive out all water. A portion of the melt was poured directly into water. One of the castings was quenched immediately in water, and the other allowed to cool slowly in the silica. In most cases a button of suitable size for polishing was obtained from the direct quenching operation.

After the castings had thoroughly cooled the molds were removed, and the castings forced out of them. With the more slowly cooled specimens this operation presented much difficulty, because of the softness of the copper, and its tendency to spread



on being hammered. In most cases this difficulty was overcome by the use of quick taps with the hammer. In a few most perverse cases the casting was left in the mold.

### (3) Method of Grinding and Polishing.

Buttons of suitable thickness, usually about a quarter of an inch, were sawed from the castings. These were ground to a smooth surface on an emery wheel, and subsequently polished successively by hand on Huberts' emery papers, 1, 00, 0000, and finally on the rouge board. The softness of the copper made it necessary to perform these operations by hand. The common method was used of polishing in one direction on one paper, and at right angles on the next until all the scratches from the former had disappeared. The greatest care had to be observed that not a particle of one size was carried over to the next. The operation of polishing the surface on the 0000 paper presented the greatest difficulty. This also had to be done by hand. The most satisfactory surface for the final polishing operation was finally obtained by sifting the rouge through a fine linen cloth, and using it sparingly over a smooth damp surface of fairly worn broadcloth. Even with this precaution the presence of scratches could not be entirely prevented. After the final operation, the buttons were placed in a dessicator and kept ready for etching.

### (4) Method of Etching.

Various reagents of varying strengths were tried: ferric chloride in hydrochloric acid, iodine in potassium iodide and in alcohol, ammonium hydroxide and hydrogen peroxide, and dilute hydrochloric and nitric acids. Nitric acid proved to be the most efficient of all. By means of a pipette a drop of the acid was





placed on the surface of the specimen, and when sufficient etching had occurred, the specimen was washed thoroughly in running water and dried before a fan.

Polishing alone was sufficient to bring out the structure in relief on almost all the specimens examined. The chromium-rich portions stood out beyond the softer copper-rich portions.

#### 4. The Apparatus and Methods used in Microscopic Study and Photographic Work.

A Leitz Metallurgical Microscope with camera attached was available for microscopic study of the specimens. All the pictures shown herein were taken with this instrument. A 250 watt tungsten lamp was fitted on the instrument in place of the original arc attachment, and, although the intensity of light from the lamp was not so great as that from the arc, the advantage of steadiness far outweighed this disadvantage.

Since the photographic methods involved are well known, and were not made the subject of any especial study, no further mention will be made of them herein.

A complete microscopic study was made of all the specimens obtained for the purpose, and only those which were representative of the composition ranges employed in the investigation were photographed. The pictures appear in the following pages.

#### 5. The Method used in the Analysis of the Alloys.

Each casting was turned in a lathe, and the turnings from a representative section were collected, washed with ether, and dried in an oven thoroughly.

The separation of copper and chromium in the sample



was effected by solution of the copper in strong nitric acid. The chromium metal was not dissolved by the nitric acid, and was separated readily from the copper solution by filtration through a Gooch crucible. The minute crystals of chromium on the filter were found to be passive toward hydrochloric and sulphuric acids; but dissolved readily on long digestion in the cold with strong hydrochloric acid.

Both copper and chromium were estimated volumetrically by the iodometric titration method.

#### 6. Results, a. Thermal Equilibrium.

Cooling curves were taken of seven melts varying in composition from 0.25% to 50% chromium in the original mixture. Temperature changes were recorded between 1600° C. and 1000° C. Throughout the greater extent of the cooling range, readings were taken each minute. Only in regions of arrest-points were readings taken oftener. Here it was found expedient to record temperatures at half-minute intervals.

Table 1, on the following page, is a record of the readings taken from the potentiometer indicator used. Immediately following each temperature is a number indicating the fall per minute at that particular temperature. The same results are shown graphically as cooling curves in Fig. 5. The curves in this figure have been plotted by an adaptation of the inverse rate method, with the temperature readings as ordinates and the rates of fall as corresponding abscissae.

The natural course of such a curve, in the absence of any arrest-points or halts caused by the evolution of heat from the cooling substance, would follow a straight line, if the rate of cooling were kept constant. In the investigation, however, this



TABLE 1

Time in min.	T ° C. .25%	dT dt	T ° C. .5%	dT dt	T ° C. 10%	dT dt	T ° C. 20%	dT dt	T ° C. 30%	dT dt	T ° C. 40%	dT dt	T ° C. 50%	dT dt
0	1545		1554		1548		1586		1595		1560			
1	1515	30	1524	30	1518	30	1554	32	1564	31	1531	29	1567	
2	1487	28	1495	29	1489	29	1524	30	1530	30	1503	28	1537	30
3	1461	26	1468	27	1462	27	1493	31	1501	29	1475	28	1508	29
4	1436	25	1443	25	1440	22	1465	26	1473	28	1469	26	1481	27
5	1414	22	1421	22	1419	21	1441	24	1447	26	1449	20	1456	25
6	1394	20	1401	20	1398	21	1417	24	1417	24	1426	23	1434	27
7	1374	20	1381	20	1376	22	1394	23	1396	26	1393	23	1355	19
8	1354	20	1361	20	1355	21	1372	22	1372	24	1369	24	1335 <sup>b</sup>	20
9	1335	19	1342	19	1335	20	1350	22	1349	23	1346	23	1316	19
10	1317	18	1324	18	1316	19	1329	21	1326	23	1324	22	1299	17
11	1300	17	1306	18	1298	18	1307	22	1304	22	1302	22	1283	16
12	1283	17	1289	17	1280	18	1287	20	1283	21	1280	22	1268	15
13	1266	17	1272	17	1263	17	1268	19	1263	20	1259	21	1251	17
14	1250	16	1256	16	1247	17	1250	18	1242	21	1238	21	1236	15
15	1235	15	1240	16	1230	17	1233	17	1222	20	1216	22	1222	14
16	1220	15	1225	15	1215	15	1216	17	1203	19	1196	20	1208	14
17	1203	17	1211	14	1200	15	1201	15	1186	17	1178	18	1197	14
18	1188	15	1197	14	1186	14	1185	16	1169	17	1161	17	1180	14
19	1175	13	1174	13	1173	13	1171	14	1154	15	1144	17	1180	14
20	1161	14	1171	13	1159	14	1157	14	1139	15	1128	16	1153	14
21	1148	13	1159	12	1146	13	1144	13	1125	14	1112	16	1140	13
22	1136	12	1146	13	1134	12	1131	13	1112	13	1097	15	1128	12
23	1124	12	1134	12	1124	10	1119	12	1099	13	1084	13	1116	12
23.5	-----	--	-----	--	-----	--	-----	--	-----	--	1078	12	-----	--
24	1112	12	1123	11	1113	11	1106	13	1087	12	1074	2	1104	12
24.5	-----	--	-----	--	-----	--	-----	--	-----	--	1073	2	-----	--
25	1100	12	1112	11	1103	10	1095	11	1077	10	1073	0	1093	11
25.5	-----	--	-----	--	-----	--	1090	10	1075	4	1073	0	-----	---
26	1089	11	1101	11	1092	11	1085	10	1073	4	1073	0	1082	11
27.5	1084	10	-----	--	1087	10	1080	10	1073	0	1073	0	-----	---
27	1079	10	1091	10	1081	12	1078	4	1073	0	1073	0	1071	11
27.5	1077	4	-----	--	1076	10	1075	6	1073	0	1073	0	1065	12
28	1076	2	1081	10	1074	4	1074	2	1073	0	1072	2	1064	2
28.5	1076	0	1077	8	1074	0	1074	0	1072	0	1071	2	1064	0
29	1076	0	1074	7	1074	0	1074	0	1072	0	1070	2	1064	0
30	1076	0	1074	0	1074	0	1074	0	1072	0	1053	24	1064	0
30.5	1076	0	1074	0	1074	0	1074	0	1072	0	-----	--	1063	2
31	1076	0	1074	0	1074	0	1073	2	1065	12	1037	16	1063	0
32	1075	2	1074	0	1073	2	1073	0	1042	23	1022	15	1062	2
32.5	1075	0	1073	2	1073	0	1272	2	-----	--	-----	--	-----	--
33	1074	2	1073	0	1073	0	1069	6	1027	15	1012	10	1040	22
33.5	1070	8	1073	0	1071	4	-----	--	-----	--	-----	--	-----	--
34	1058	24	1073	6	1060	22	1045	24	1015	12	1001	11	1032	18
35	1042	16	1047	23	1045	15	1027	18	996	9	989	12	1018	14
36	1030	12	1030	17	1032	13	1013	14	-----	--	-----	--	-----	--
37	1020	10	1018	12	1020	12	1002	11	-----	--	-----	--	-----	--
38	1010	10	1008	10	1009	11	-----	--	-----	--	-----	--	-----	--
39	1001	9	1000	8	-----	--	-----	--	-----	--	-----	--	-----	--
40	989	11	990	10	-----	--	-----	--	-----	--	-----	--	-----	--

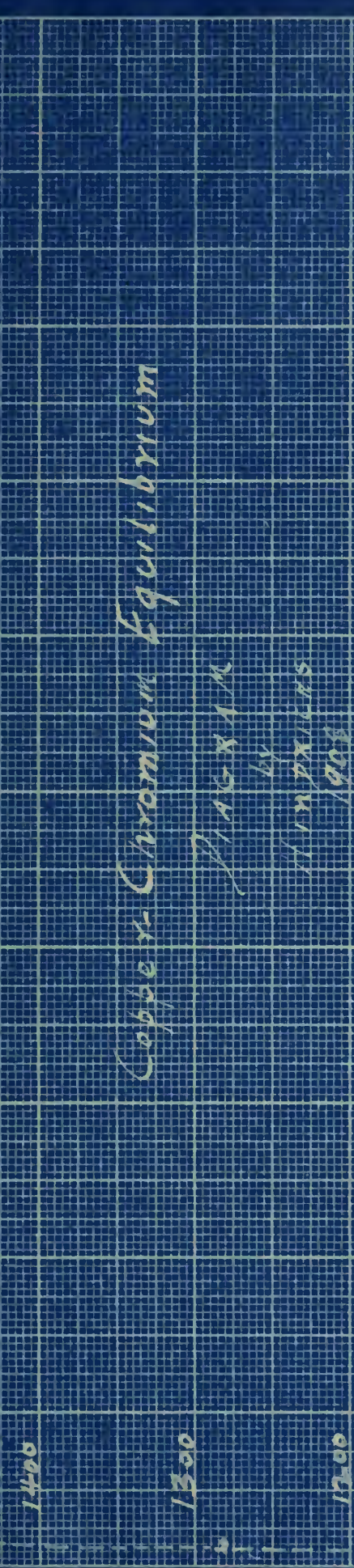
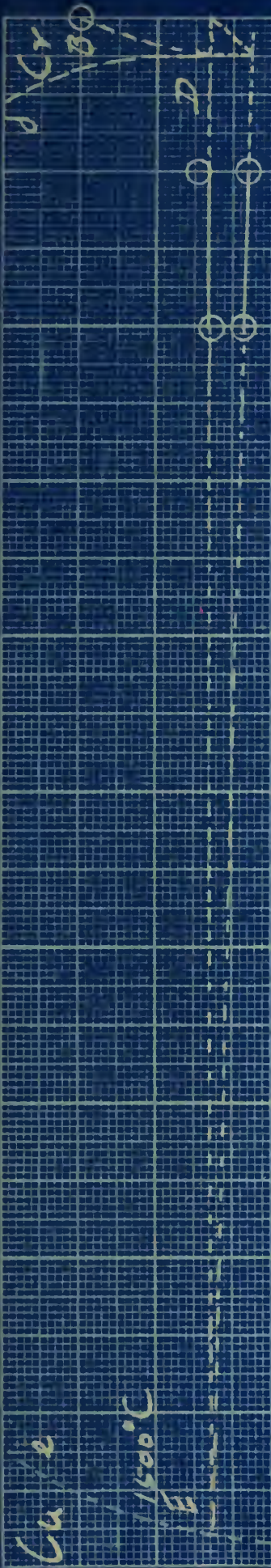


very desirable condition could not be realized. The furnace was allowed to cool by radiation to the atmosphere, and its environment was kept as constant as possible for all readings. Naturally, under these conditions, the rate would be faster at higher temperatures and slower at lower temperatures. The curve should then slope gradually to the left toward the vertical axis. Any quickening in the rate of cooling would show up as a steeper portion; and on the contrary, any lag in cooling would appear in the curve as a less steep portion. If the heat effect in the cooling mass were great enough, a more or less sharp angle in the direction of the vertical axis should be expected in the curve at the temperature at which the cooling was retarded. Naturally enough, one could not expect ideal curves with the apparatus used, since the rate of cooling could not well be kept under complete control. But with the size of melts used, it was hoped, and fairly well realized, that the changes in the rate of cooling due to the effect of momentary changes in the environment would show up as only minor jogs in the plotted curves.

The curves in Fig. 5. are for the most part fairly regular. The curve for 0.25% chromium shows no definite arrest point until the temperature of  $1076^{\circ}\text{C}$ . is reached. Here the curve touches the vertical axis, indicating thereby that at this temperature there is no fall in temperature. When the temperature falls again, the rate of cooling is quite rapid for the minute or two following the time of the arrest; then it gradually assumes the normal value for the temperature in question. This is noticeable in all the curves in the figure, and is fairly constant in magnitude. The second curve, for 0.5% chromium, shows a slight arrest at  $1390^{\circ}\text{C}$ . and a very



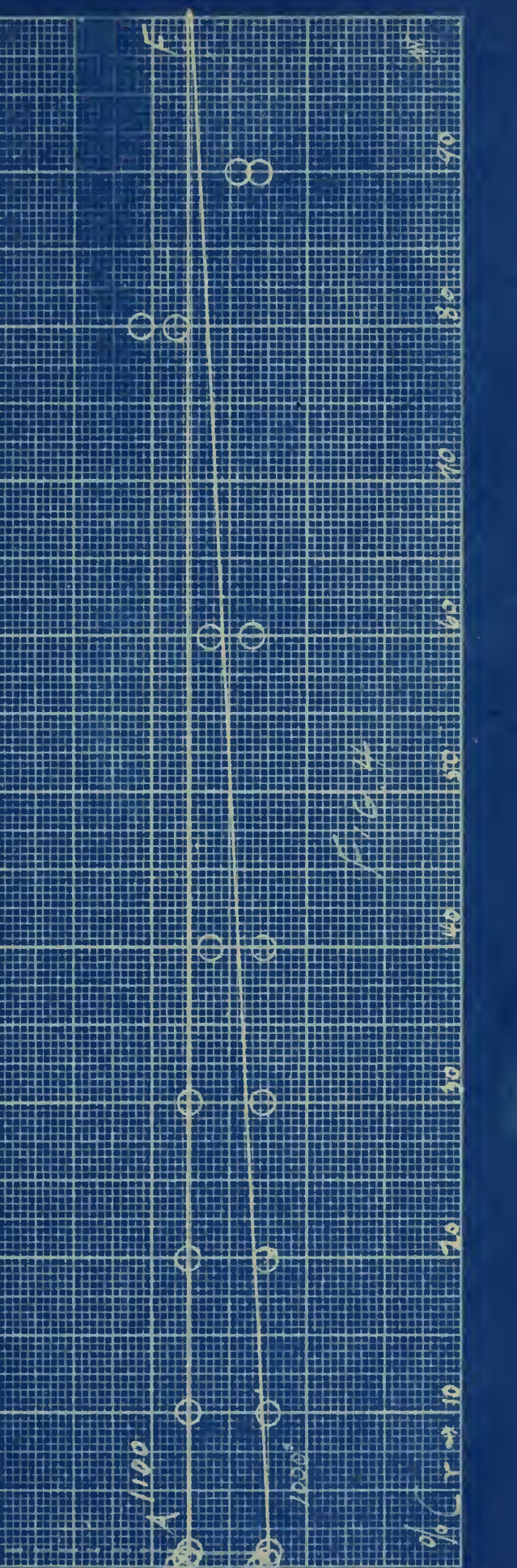




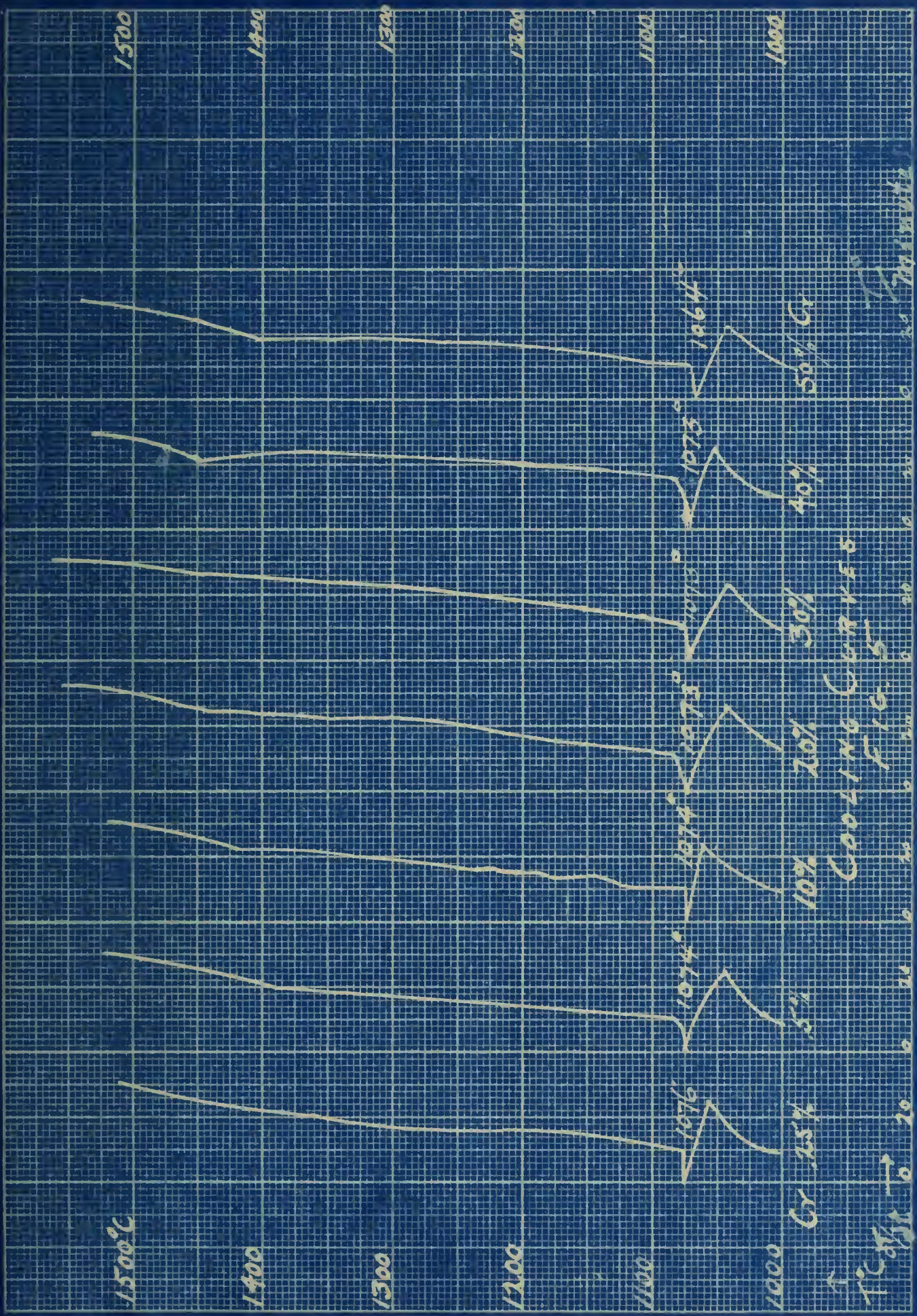
Copper-Chromium Equilibrium

1/10 x 1/10

1/10 x 1/10







67-75%  
 10%  
 30%  
 40%  
 50%  
 1976  
 1977  
 1978  
 1500°C  
 1400  
 1300  
 1200  
 1100  
 1000



definite one at  $1074^{\circ}\text{C}$ . The curves for the melts of higher chromium content have more or less well defined arrest-points as indicated in the figure. It is to be noted that in almost every case below the upper arrest-point the curve slopes more quickly toward the vertical axis, indicating thereby a slowing in the rate of cooling. This is evidently due to the heat effect of the crystallization of the excess chromium.

Figure 6 is a graphical summation of the data from the curves. In this figure the temperatures appear as ordinates, and the initial percent composition of the melt by weight as the corresponding abscissae. The arrest points are plotted for each concentration. The temperatures in Fig. 6 are plotted one degree higher than those which appear in the curves in Fig. 5, the correction being necessary because of the previous calibration of the instrument. All the points in the graph surrounded by circles represent points actually determined by thermal methods with the exception of point J. This point denotes the maximum solubility of molten chromium in molten copper, and was determined by heating a mixture of equal portions of copper and chromium in a furnace at its maximum temperature (approximately  $1600^{\circ}\text{C}$ .) for several hours, and analyzing the cooled mixture. The data for this melt will be found in Table 2.

Figure 6 may be regarded as a summary of the thermal data obtained in this investigation. It covers the region from pure copper to fifty percent chromium content. The line BDG ( $1075^{\circ}$ ) represents the arrest in cooling caused by the solidifying of the eutectic. The upper dashed line ( $1468^{\circ}$ ) is not so well established. However, in conjunction with the data obtained from Fig. 4, Hindrichs' diagram, for melts of compositions 80% and 90% chromium,









respectively,  $1468^{\circ}\text{C}$ . may be regarded as very probably the correct temperature for its location. The data obtained do not warrant any definite statement as to the course of the line BIJ between the two well established points B, and J. A typical system of partially immiscible metals, however, would evidently demand a triple point at I, and hence we might expect an angle in the line BJ at some point, I, along the line IH. This point cannot be located from the data so far obtained.

The diagram cannot be accepted without some further reservations. First, the percent compositions as plotted represent the initial weight percent of the mixtures used. As pointed out by Harder, however, the chromium content of the melt decreased considerably in the course of melting, by oxidation and slagging off. This was found to be very true later in this investigation as well. Because of the mixing of the layers in the melt and the inclusion of foreign particles, no representative analysis of the mixtures could be made. Secondly, the arrest points in the curve for 50% chromium content are considerably lower than one would expect. The cooling curve for this melt was taken with the use of a graphite protecting tube in the manner already stated. The gases arising from the oxidation of the graphite were evidently occluded with considerable rapidity by the thermo-couple, with consequent change in resistivity. An attempt to determine the extent of this effect by calibrating against a quartz protecting tube resulted in failure, due to the repeated breaking of the platinum-rhodium element of the couple when used in the graphite tube. The points in question cannot be accepted as accurate, and are valuable only in indicating the general position of the arrest-points.

It is to be noted that these results, in so far as they



extend, and with the exceptions mentioned, confirm the results of Hindrichs. (See Fig. 4).

The system, copper-chromium, above  $1468^{\circ}\text{C}$ . is a two phase system throughout the greater extent of its concentrations range. A melt of equal portions, for instance, at a temperature of  $1600^{\circ}\text{C}$ . would consist of two layers, an upper layer of chromium saturated with copper and a lower one of copper saturated with chromium. Harder succeeded in obtaining such a separation. If heat were abstracted from the system, the composition in each layer would follow the lines  $dD$  and  $eE$  (Fig. 4) or  $JI$  (Fig. 6). At point  $D$  (Fig. 4) crystals of chromium or a chromium-rich constituent begin to form in the upper layer. The temperature would remain constant until the layer is solidified. Further abstraction of heat would cause the precipitation of more chromium from the lower layer, the composition of the mother liquor following down  $IB$  (Fig. 6) until the temperature of  $1075^{\circ}\text{C}$ . is arrived at. The temperature would remain constant at this point while the eutectic crystallized, and thereafter fall gradually.

If such an interpretation as given in Fig. 4 is to be accepted, only one eutectic can be present in the system, and not two as Hindrichs supposes. From a consideration of the phase rule, the point  $D$ , Fig. 4, represents not a triple point at which two crystalline phases and one liquid phase are in equilibrium--a condition which would allow the formation of a eutectic,--but a triple point at which two liquid phases are in equilibrium with a crystalline phase,--a condition which would surely not allow the formation of a eutectic. At this point a liquid phase consisting of copper saturated with chromium, composition  $E$ , another liquid phase of chromium saturated with copper, composition  $D$ , and



a solid phase consisting of crystals of copper which have separated along the line BD, are all in equilibrium. The line DE would represent, not the crystallization of a eutectic, but the solidification of the liquid phase of chromium rich in copper, probably as a solid solution. In the absence of confirmation from a microscopical study of the structure, this point can not of course be established with certainty.

Further interpretation of the diagram is evidently a matter of knowledge of the phase rule and its application, and will not be continued here.

#### b. Chemical Analysis.

The table on the following page gives in convenient form the results of the analyses of the alloys prepared for microscopic study.

It will be noted, on examination of the table, that the percent of chromium, as determined by analysis of the alloy casting, is invariably lower than the initial percent of chromium in the mixture. The difference is not constant. The loss is evidently due to the slagging off of the oxidized chromium. Such a result should cause hesitancy in accepting any data based on weights used in the initial mixture.

#### c. Microstructure.

The study of the microstructure confirms the presence of a eutectic between 0.43 and 0.31% chromium content. The eutectic structure is shown remarkably well in Figs. 12 to 15, and it consists of polyhedral crystal grains of copper, within which, arranged regularly, are rods of chromium. In the pictures these rods appear as dots when cut cross-wise. The hypo-eutectic



TABLE 2

Melt No.	Casting No.	Weight of Melt	Weight of Cu	Weight of Cr	Weight percent (Initial) Cu	Weight percent Cr	Weight percent (by analysis) Cu	Weight percent Cr	Percent Impurities
1	005	600	597.0	3.0	99.5	0.50	98.51	0.46	1.03
2	0075	600	595.5	4.5	99.25	0.75	98.76	0.16	1.08
3	010	600	594.0	6.0	99.0	1.00	Not analyzed		
4	015	600	592.5	7.5	98.5	1.5	98.42	0.43	1.15
5	020	600	588	12	98.0	2.0	99.27	0.31	0.48
6	030	600	582	18	97.0	3.0	96.35	2.46	1.19
7	040	600	576	24	96.0	4.0	Not analyzed		
8	050	600	570	30	95.0	5.0	97.03	2.61	0.36
9	070	600	558	42	93.0	7.0	Not analyzed		
10	090	700	637	63	91.0	9.0	94.40	4.69	0.91
11	110	500	445	55	89.0	11.0	94.33	4.83	0.84
12	130	600	522	78	87.0	13.0	90.45	8.10	1.45
13	150	600	510	90	85.0	15.0	89.99	9.37	0.74
14	200	600	480	120	80.0	20.0	Not analyzed		
15	250	600	450	150	75.0	25.0	92.13	7.40	0.47
16	500	100	50	50	50.0	50.0	87.29	12.64	0.07

Note.--The values appearing in the last column of the table are obtained by difference. A qualitative analysis showed that the impurities consist of slight traces of aluminum, iron, and silica. Microscopic examination showed mechanically included slag and particles of carbon.





composition in Figs. 9 to 11 shows excess copper, while all the hyper-eutectic compositions show excess chromium, which has crystallized out in the dendritic form. In some specimens of higher composition, the eutectic does not appear without etching. Etching also defines the large crystalline grains nicely. The size of these is decreased with the increase of chromium and with quenching.

In no specimens studied with the microscope could evidence of an emulsion be found. The crystals of excess chromium in all instances are quite well formed and complete, and bear every evidence of having crystallized out of solution on slow cooling, rather than having been formed from a drop of chromium suspended in molten copper. In support of this statement might also be mentioned the fact that the quenched specimens invariably show similar structure to the corresponding specimens which have been cooled slowly. If the chromium were present in suspension, there is no reason why the crystals of chromium should not be almost the same in size regardless of the manner in which the specimen was treated in cooling. There is no doubt that emulsions can occur when the two liquid phases are present and an adequate length of time is not given for complete separation. The conclusion must then be drawn, that the method of long heating used in this investigation has prevented the formation of emulsions in the series studied.

#### 7. Metals used in Preparation of Alloys.

The copper used in the investigation was Liner and Amend's electrolytically refined copper in shots, and was 99.8% pure. The chromium metal used was obtained from the Goldschmidt Thermit Co., and was 98.95% pure. The impurities were  $\text{Cr}_2\text{O}_3$ , Al, Fe, in traces.



### III. Summary.

1. A gas furnace was developed which gave a fairly adequate range of temperature for the thermal study of the alloys of copper and chromium.

2. Cooling curves of seven mixtures were taken, but the mixtures were not analyzed.

3. Sixteen alloys were prepared and cast. Most of these have been analyzed and those of representative composition have been studied with the microscope and photographed.

### IV. Conclusions.

1. The results of Hindrichs in regard to thermal data have been confirmed in the main in the region below fifty percent chromium content. No data were obtained above that composition in this investigation. Throughout the range studied the two metals exhibit the characteristics of partially immiscible metals.

2. The system has a eutectic between 0.46 and 0.43% chromium content. This is probably the only eutectic in the system.

3. The maximum solubility of chromium in copper at approximately  $1600^{\circ}\text{C}$ . is 12.64%.

4. Above the temperature of  $1468^{\circ}\text{C}$ . there is a region, as yet poorly defined, in which the molten system consists of two phases, a layer of chromium saturated with copper, and a layer of copper saturated with chromium. It is quite doubtful that the temperature of boiling copper is outside of this region.

5. The solubility of chromium in solid copper is very slight.

6. No solid solutions are in evidence below the composition of 12.64% chromium.





Fig. 7 Cu-Cr w. 0.16% Cr.  
Cooled slowly. Etched w.  
dil.  $\text{HNO}_3$ . Polyhedral  
crystals from center of  
specimen. x80.



Fig. 8 Cu-Cr w. 0.16% Cr.  
Same as Fig. 7. x210.



Fig. 9 Cu-Cr w. 0.31% Cr.  
Cooled slowly. Unetched.  
Hypo-eutectic w. excess  
Cu. x80.

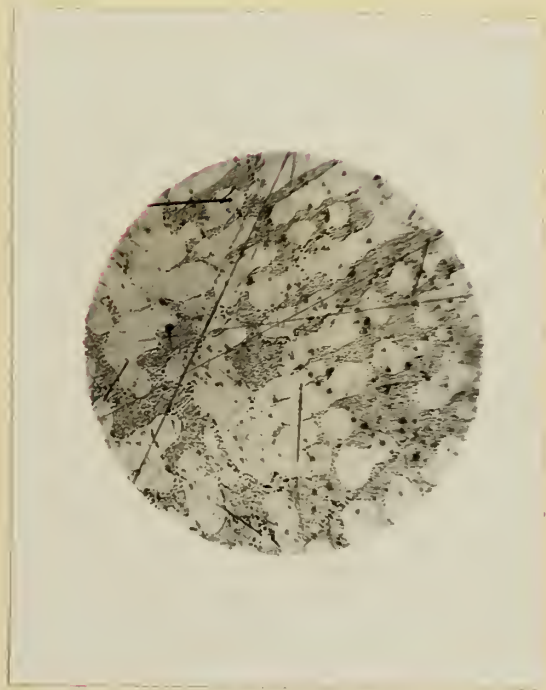


Fig. 10 Cu-Cr w. 0.31% Cr.  
Quenched. Unetched. Hypo-  
eutectic. x80.



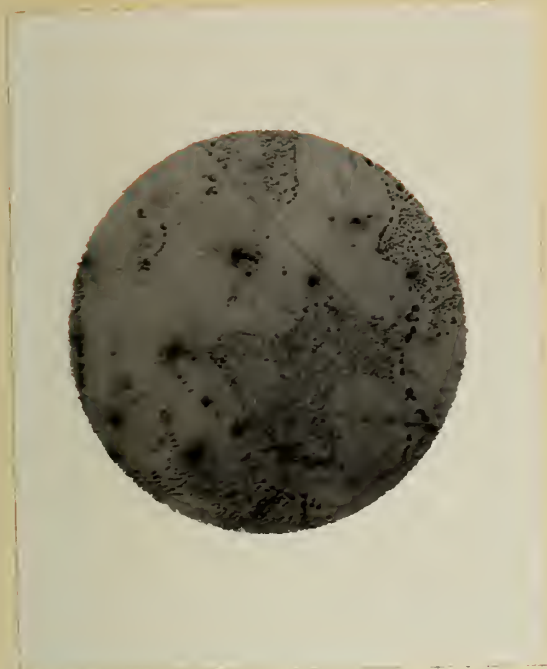


Fig. 11 Cu-Cr w. 0.31% Cr.  
Quenched. Same as Fig. 10.  
x210



Fig. 12 Cu-Cr w. 0.43% Cr.  
Cooled Slowly. Etched w.  
 $HNO_3$ . Structure near eu-  
tectic. Large crystalline  
grains on outer edge. x210.



Fig. 13 Cu-Cr w. 0.43% Cr.  
Same as in Fig. 12. x210.



Fig. 14 Cu-Cr w. 0.43% Cr.  
From same specimen as Fig.  
12. x210.







Fig. 15 Cu-Cr w. 0.43% Cr.  
Showing rod-like structure  
in eutectic. x210.



Fig. 16 Cu-Cr w. 0.46% Cr.  
Quenched. Etched w. dil.  
 $\text{HNO}_3$ . Showing boundaries  
of crystalline grains. x80.



Fig. 17 Cu-Cr w. 0.46% Cr.  
Same as Fig. 16. Quenched.  
Etched w.  $\text{I}_2$  in  $\text{C}_2\text{H}_5\text{OH}$ . x80

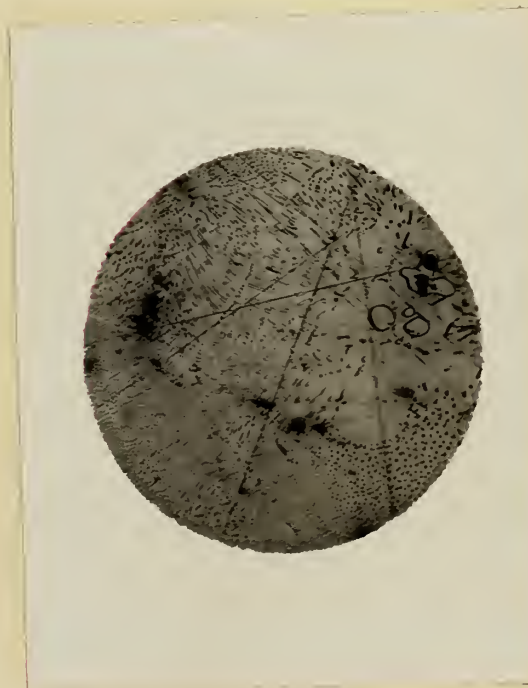


Fig. 18 Cu-Cr w. 0.46% Cr.  
Same as Fig. 16. Quenched.  
Outer edge. x210.



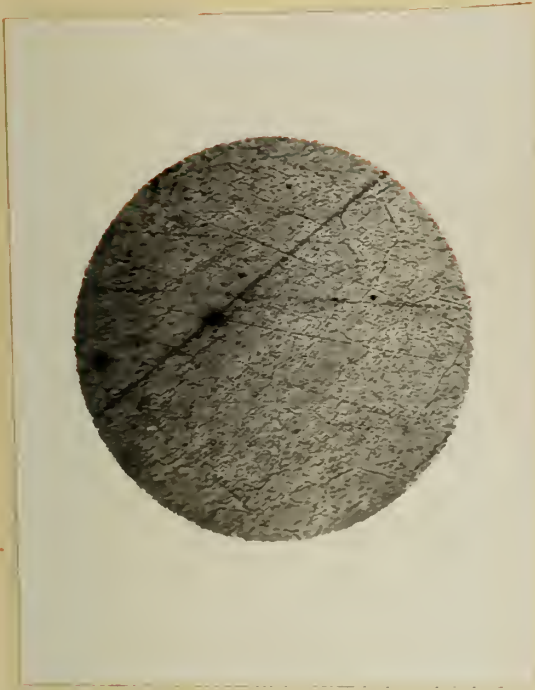


Fig. 19 Cu-Cr w. 0.46% Cr. Same as Fig. 16. Center of specimen. Unetched. x80



Fig. 20. Cu-Cr w. 2.61% Cr. Cooled slowly. Hyper-eutectic structure. Porous. Excess chromium showing. x80.



Fig. 21. Cu-Cr w. 4.69% Cr. Quenched from molten state by pouring directly into water. x80.



Fig. 22 Cu-Cr w. 4.83% Cr. Cooled slowly. Unetched. Well formed dendrites of Cr. x80.





Fig. 23 Cu-Cr w. 4.83% Cr.  
Cooled Slowly. Same as in  
Fig. 22. x210.

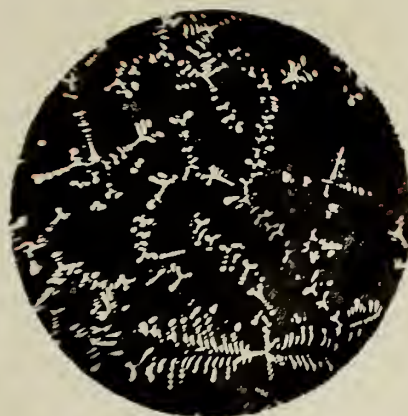


Fig. 24 Cu-Cr w. 7.40% Cr.  
Cooled slowly. Etched with  
dil  $\text{HNO}_3$ . Well formed den-  
drites of chromium. Eutectic  
matrix. x80.

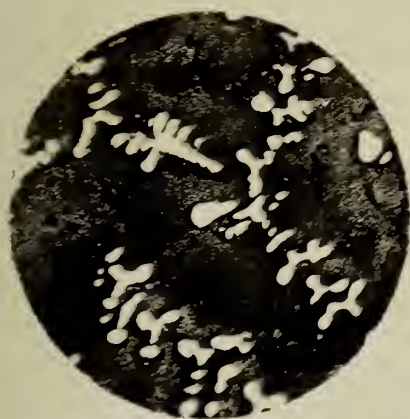


Fig. 25. Cu-Cr 7.40% Cr.  
Same as in Fig. 22. x210.



Fig. 26 Cu-Cr w. 9.37% Cr.  
Cooled slowly. Etched w.  
dil.  $\text{HNO}_3$ . x80.



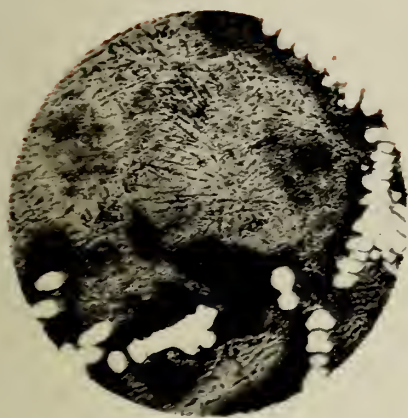


Fig. 27 Cu-Cr w. 9.37% Cr.  
Same as in Fig. 26. x210.



Fig. 28 Cu-Cr w. 12.64% Cr.  
Unetched. Specimen from Cu  
layer of melt of equal por-  
tions Cu and Cr cooled slow-  
ly. x80.



Fig. 29 Cu-Cr w. 12.64% Cr.  
From same specimen as Fig. 28.  
Showing a particularly large  
dendrite of Cr. cut length-  
wise. x80

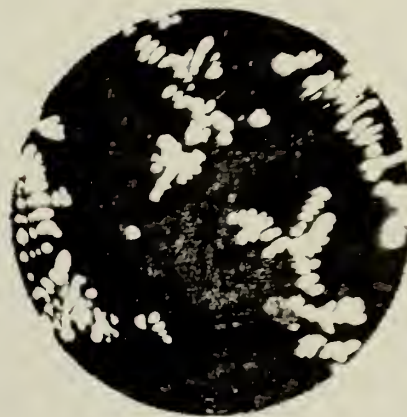


Fig. 30 Cu-Cr w. 12.64% Cr.  
From same specimen as Fig.  
28. Etched with dil.  $\text{HNO}_3$ .  
Eutectic showing. x80.







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