SOLUBILITY OF CARBON IN MOLTEN COPPER-MANGANESE AND COPPER-NICKEL ALLOYS

By

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INTRODUCTION

Although maximum carbon contents are specified for several of the commercial copper-base alloys, no information is available on the equilibrium solubility of carbon in these alloys. The solubility of carbon in molten pure copper has recently been investigated by Bever and Floe.(1) It is desirable to obtain similar data for the alloys of copper.

In the production of copper alloys carbonaceous covers and crucibles are sometimes used. If even small quantities of carbon are in solution, insoluble carbon oxide gases may be formed when the metal is poured under oxidizing conditions. This is known to be a cause of gas porosity in casting certain copper-base products.(2)

Any carbon present in the solidified alloy will also have a direct effect on physical properties. If the carbon is precipitated out as graphite it disrupts the metallic matrix and the structure may be similar to grey cast iron. If the carbon forms an alloy carbide such as manganese carbide, the carbides may have an embrittling or strengthening effect on the alloy.

Among the copper-base alloys, those of copper and manganese and copper and nickel are of practical importance as they are widely used either as binary alloys or as a base for more complex alloys. Published data in the literature show that molten manganese and nickel dissolve fairly large amounts of carbon. There is no theoretical basis for predicting to what extent these metals retain their ability to dissolve carbon when they themselves are dissolved in molten copper.

I REVIEW OF PREVIOUS WORK

The solubility of carbon in molten pure copper has been found to be about 0.0001 per cent carbon at 1100° C and 0.0004 per cent at 1475° C.(1) The solubility of carbon in manganese has been established by various investigators(3),(4),(5),(6)) to be about 6.7 per cent carbon at 1217° C. It does not change a great deal with temperature.

Corson(7) found indications that carbon is soluble in copper-manganese alloys. He states that alloys up to 30 per cent manganese can be made satisfactorily in any type of furnace but that alloys which have been protected from the fuel gases will have considerably higher ductility. Also the ductility of those made in graphite or fire clay crucibles will be less, which Corson attributes to the absorption of carbon. He states that the alloys absorb carbon in proportion to their manganese content. According to Corson at 30 per cent manganese as much as 0.20 per cent carbon may be expected in an alloy made in a graphite crucible and stirred with a graphite bar, while continuous contact with charcoal will cause the absorption of about 0.50 per cent carbon. Corson states that in this case the alloys become cold short. He refers to their structure as "biscuit structure". Corson gives no information on the temperature of the molten metal and on the method of carbon analysis.

Dean and his associates(8),(9),(10),(11)) have worked extensively on copper-manganese alloys. They state that these alloys are melted in alundum crucibles. Apparently they wanted to avoid carbon absorption by the metal.

The solubility of carbon in nickel has been investigated by Ruff and his collaborators(12),(13),(14)) and by Kase.(15) The hypereutectic liquidus has a moderate slope and reaches 3 per cent carbon at about 1750° C. Ruff and Martin(13) extended their investigation to very high temperatures and found a solubility of about 6.42 per cent carbon at 2100° C. Above this temperature the solubility was found to remain constant up to 2500° C.

Mishima(16) investigated the influence of carbon on the behavior of nickel and its alloys during annealing. He concluded that annealing nickel-copper alloys between 700° C and 900° C promotes the precipitation of free carbon in the grain boundaries and causes "annealing brittleness".

II EXPERIMENTAL METHODS

The present investigation was carried out by saturating samples of molten copper-manganese alloys and copper-nickel alloys. The samples were then analyzed for total carbon present by the classical combustion method.

1. Preparation of Samples

In order to retain any dissolved carbon quantitatively in the metal, the samples had to be prepared by rapid quenching from the saturation temperature. Direct contact of the melt with air, water, steam and the oxides of carbon was undesirable. In order to decrease the danger of mechanical inclusion of graphite it was not advisable to pour the melt over graphite. Therefore a method of water quenching in which the metal remains under a protective atmosphere as described by Bever and Floe(1) was used.

This method combines the fast quenching action of water with the protection of an inert atmosphere. A crucible (8 inches long by 3/4 inches in outside diameter) was suspended in a vertical tube furnace through which an inert gas (nitrogen or argon) was passed. The crucible was suspended so that it could be released and fall freely into a container of cold water placed directly under the furnace tube. In quenching the crucible came to rest with its top projecting inside the furnace and the melt was thus protected by the inert atmosphere maintained in the furnace tube.

The quenching action seemed to be effective and the metal solidified in a few seconds. Rough observations indicated that the bath solidified completely in less than five seconds. Moreover, the freezing process has the desirable characteristic of starting simultaneously along the entire surface of the sample and thus tends to retain quantitatively any dissolved carbon.

The details of the furnace construction are shown in Figure 1. It consisted of a silica tube (30 inches long and $1\frac{1}{2}$ inches in outside diameter) over which a brass head C fitted tightly. This head supported the pin I on which the crucible was suspended and had a tube connection B through which the inert gas was introduced into the furnace.

Prepurified dry nitrogen was used for all samples except those high in manganese (numbers 25 to 38 inclusive). Information received from the supplier indicated that the oxygen and hydrogen contents of the nitrogen were less than 0.002 per cent. The high manganese samples were made under argon which according to the supplier analyzed 99.9 per cent argon and 0.1 per cent nitrogen.

The crucibles were machined from graphite rods of very high purity*. The samples which dissolved more than 0.10 per cent carbon undercut the crucible walls so that the crucible had to be broken in order to extract the solidified sample. Therefore, it was necessary to use a new crucible for each sample containing more

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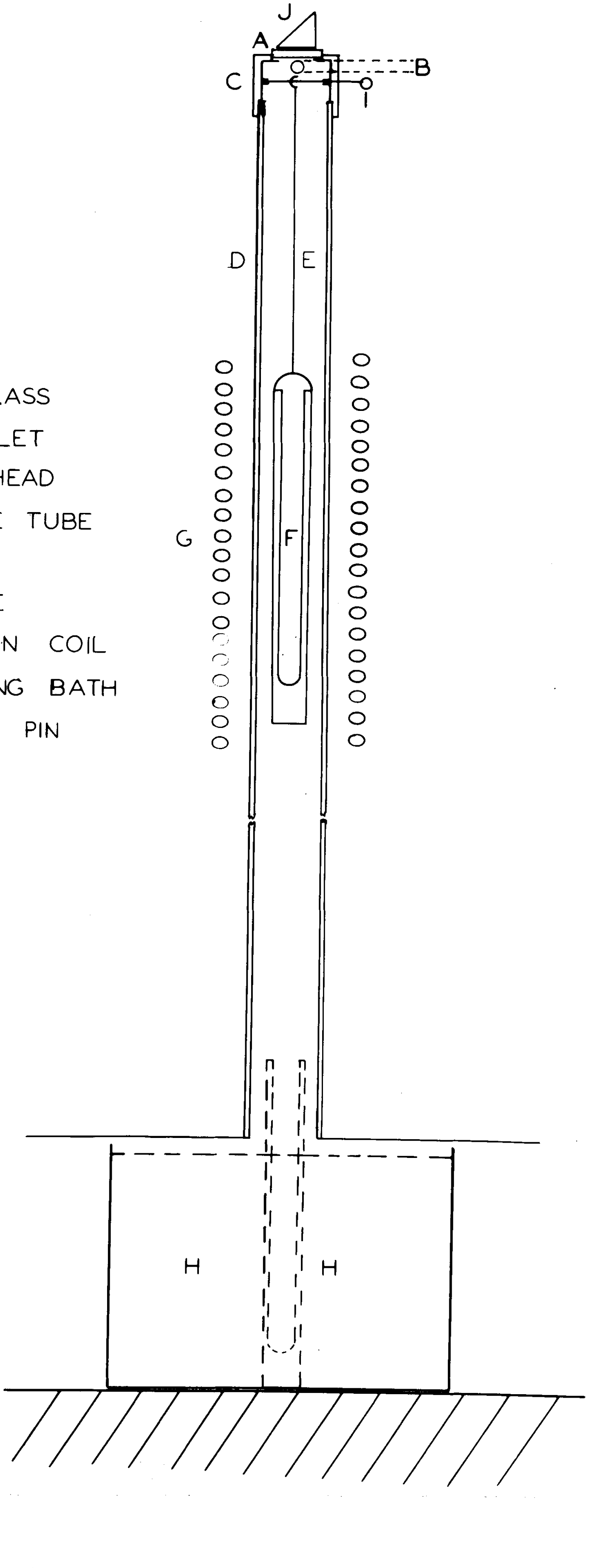
* AGT and AGX grades. National Carbon Company, Cleveland, Ohio



A = SIGHT GLASS
B = GAS INLET
C = BRASS HEAD
D = FURNACE TUBE
E = WIRE
F = CRUCIBLE
G = INDUCTION COIL
H = QUENCHING BATH
I = RELEASE PIN
J = PRISM

Figure 1. Schematic View of Furnace used in Preparing Samples.

than 25 per cent of manganese or nickel. In order to get the best quenching action the thickness of the crucible wall was kept to a minimum. The very high-manganese samples dissolved so much of the crucibles that their wall thickness had to be doubled in order to insure against the possibility of dissolving the entire wall thickness.

The manganese used was the high-purity electrolytic metal prepared by the U. S. Bureau of Mines. This manganese can be considered to be 99.95 per cent pure. Principal impurity is sulphur and others next in order of occurrence are small amounts of iron, nickel, molybdenum, lead, arsenic, copper, with a trace of carbon. The metal as received also contains about 0.015 per cent hydrogen.

The electrolytic nickel furnished by the International Nickel Company had the following nominal analysis:

Co	0.7 %	Cu	0.01 - 0.03 %	Fe	0.01 - 0.04 %
Si	Trace	C	Trace	S	Trace

The copper used was special high purity rod prepared by the continuous casting process described by Smart, Smith and Phillips.(17) These rods had been made and analyzed in the investigation by Bever and Floe.(1) They contained smaller amounts of carbon than the alloys made from them in the investigation reported here. This carbon was not objectionable in the present investigation.

The metals were cut into shapes that could be charged to the crucible. Copper and nickel pieces were cleaned with 1:1 hydrochloric acid before weighing and charging.

The alloys were made by adding calculated and weighed amounts of manganese or nickel to weighed amounts of copper. The electrolytic manganese could easily be broken down into very small pieces which allowed the addition of exactly the required quantity to make an even alloy percentage. The weighing was done to the nearest one hundredth of a gram. Since the sample weight was about 40 grams the charge analysis was correct within 0.025 per cent. It was more difficult to comminute the nickel and consequently it was not possible to charge even percentages of nickel. However, as can be seen in Table 2 the alloy contents could be attained in the desired ranges. The metal pieces were arranged in the crucible to allow easy melting.

Temperatures were measured with a Leeds and Northrup disappearing filament pyrometer sighted on the surface of the bath through the prism J and the sight glass A in the furnace head. Since the metal occupied only a fraction of the total height of the crucible, black-body conditions were approached. The pyrometer was calibrated several times against the melting point of copper.

The procedure in making a run consisted of suspending the crucible and charge by a molybdenum wire E on the release pin I. The inert gas was turned on and allowed to flow out of the open end of the furnace tube. The power was then turned on and the charge melted and brought to temperature. After being held at this temperature long enough to reach equilibrium, the crucible was dropped into the quenching bath by withdrawing the release pin.

Some of the samples had fairly deep pipes. The metal surrounding the pipe was drilled out to eliminate any graphite particles that were likely to have collected there. As the amount of alloying element was increased the amount of adhering graphite also increased. The exterior of the sample was machined to remove all of the graphite. After machining the samples were cleaned in hot 1:1 hydrochloric acid and a section comprising one-half the cross sectional area was milled from along the entire length of the sample. The chips were carefully collected for analysis of carbon content. The remainder of the sample was retained for microscopic examination and is now available for heat treatment.

2. Method of Analysis

The method by which the samples were analyzed for carbon was based on the oxidation of carbon to carbon dioxide and the quantitative determination of this gas. This was carried out by the classical combustion analysis developed for the determination of carbon in iron and steel.

The equipment used consisted of a tube furnace through which a stream of oxygen could be passed. The exit gases were passed through a chromic acid bubble tube and a drying tube filled with dehydrite (anhydrous magnesium perchlorate). They then passed to a U-tube filled with ascarite.

The procedure for making an analytical run was as follows. The electric element heating the furnace was turned on and the furnace was allowed to come to a temperature of about 1150° C to

1200° C. Oxygen was passed through the system until the gain in weight of the ascarite tube in fifteen minutes was zero as determined on a sensitive balance. Then a known weight of the sample millings was placed into the furnace on an alundum boat. The samples weights used were 1/2 factor weight (1.3635 grams) for the high carbon samples, and 1 or 2 factor weights (2.7273 and 5.4546 grams respectively) for the low carbon alloys. The system was then closed and oxygen passed through the furnace for fifteen minutes to burn all of the carbon to carbon dioxide. The carbon dioxide was absorbed by the ascarite and the increase in weight of the U-tube was measured to one-tenth of a milligram. The increase in weight of the ascarite tube was multiplied by 20 for the 1/2 factor weight sample and by 10 or 5 for the 1 and 2 factor weight samples respectively. The resulting product was the carbon content of the samples in per cent.

III RESULTS OF EXPERIMENTAL WORK

Table 1 lists the conditions of saturation and the carbon content of the samples of copper-manganese alloys. Table 2 gives the same information for the copper-nickel alloys. Table 3 gives data on the carbon content of pure manganese samples. The stated time of saturation represents the period during which the sample was at the indicated temperature. The sample often was molten for from 10 to 20 minutes longer while the temperature was being adjusted to the desired point.

Figure 2 shows the carbon contents of the copper-manganese alloys as a function of the manganese content for several temperatures. Figure 3 shows similar information for copper-nickel alloys. Figure 4 shows the carbon contents of manganese as a function of the temperature. This figure also presents the results reported by Ruff and Bormann(6) for comparison.

Data shown in brackets in the tables are not included in Figures 2, 3, and 4. This does not mean that these data are to be considered unreliable, except for sample number 29, but it was not convenient to include them in the figures. Plotting the values for 1277° C would have resulted in a curve almost coinciding with that of 1262-1265° C. The values for samples 18 and 19 would have interfered with the 1262-1265° C curve. Values for samples 12, 13, and 33 were not plotted as the samples were checks. In Figure 2 one curve is drawn through values for 1262° C and 1265° C. It had been intended to saturate all samples at the same temperature but due to an error the two temperatures were used. It can be seen from the plotted values that this small temperature discrepancy has no measurable effect on the carbon analysis.

It must be kept in mind that the reported carbon values represent the carbon content of the solidified alloy, while the percentages of manganese and nickel represent the composition of the alloys before they absorbed carbon. For example, the alloy analyzing 50 per cent copper and 50 per cent manganese absorbed 0.839 per cent carbon, therefore, the manganese content of the solidified ternary alloy was equal to

$$\frac{50}{100.839} = 49.58 \text{ per cent}$$

There is little reason to prefer either basis of calculation provided it is realized which basis is being used.

TABLE NO. 1

Carbon Content of Quenched Samples of Copper Manganese Alloys

Sample Number	Per Cent Manganese	Conditions of Saturation		Per Cent Carbon
		Temp. °C	Time Min.	
18	5.0	1090	30	(0.0075)
19	10.0	1090	30	(0.0105)
20	15.0	1090	30	0.0250
21	20.0	1090	30	0.0360
23	25.0	1090	36	0.0550
24	32.5	1090	36	0.1360
25	40.0	1090	40	0.301
26	50.0	1090	35	0.627
32	60.0	1090	30	1.093
22	1.0	1262	32	0.0013
14	2.0	1262	30	0.0028
15	4.0	1262	30	0.0063
8	5.0	1262	35	0.0090
9	15.0	1262	35	0.041
13	15.0	1262	100	(0.039)
10	25.0	1262	35	0.141
12	25.0	1262	90	(0.142)
16	30.0	1262	30	0.263
17	40.0	1262	30	0.532
11	50.0	1262	30	0.839

Table 1, continued

Sample Number	Per Cent Manganese	Conditions of Saturation		Per Cent Carbon
		Temp. °C	Time Min.	
53	10.0	1265	30	0.023
54	20.0	1265	30	0.072
30	35.0	1265	35	0.394
33	35.0	1265	100	(0.389)
27	60.0	1265	30	1.328
28	75.0	1265	30	2.358
31	82.5	1265	40	3.760
29	100.0	1265	30	(6.319)
34	100.0	1265	60	6.749
6	10.0	1277	30	(0.024)
7	20.0	1277	30	(0.073)
5	33.0	1277	30	(0.325)
3	37.0	1277	40	(0.421)
2	48.5	1277	30	(0.768)

Values in brackets, ( ), not plotted in Figure 2.

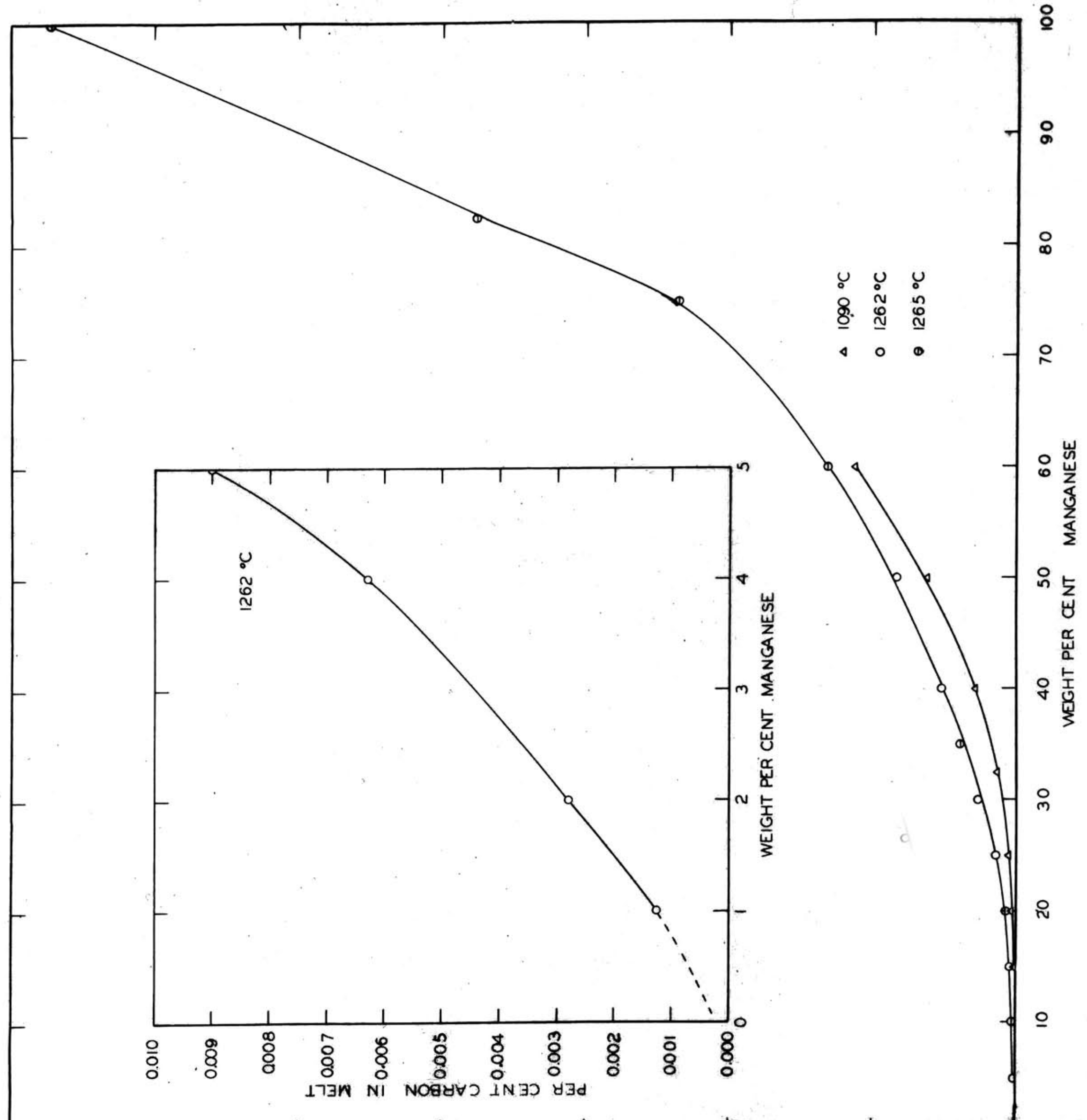


Figure 2. Solubility of Carbon in Molten Copper-Manganese Alloys as a Function of Manganese Content.

TABLE NO. 2

Carbon Content of
Quenched Samples of Copper-nickel Alloys

Sample Number	Per Cent Nickel	Conditions of Saturation		Per Cent Carbon
		Temp. °C	Time Min.	
1	25.17	1331	20	(0.154)
39	1.007	1475	30	0.0020
40	1.993	1475	30	0.0040
41	4.079	1475	35	0.0075
42	5.278	1475	30	0.013
43	9.940	1475	30	0.053
44	19.990	1475	30	0.115
45	30.191	1475	30	0.262
47	40.069	1475	30	0.543
48	49.913	1475	30	0.723
46	60.123	1475	30	1.009
51	69.285	1475	30	1.308
49	79.995	1475	30	1.724
52	90.672	1475	30	2.059
50	100.000	1475	30	2.369

Value in brackets, ( ), not plotted in Figure 3.

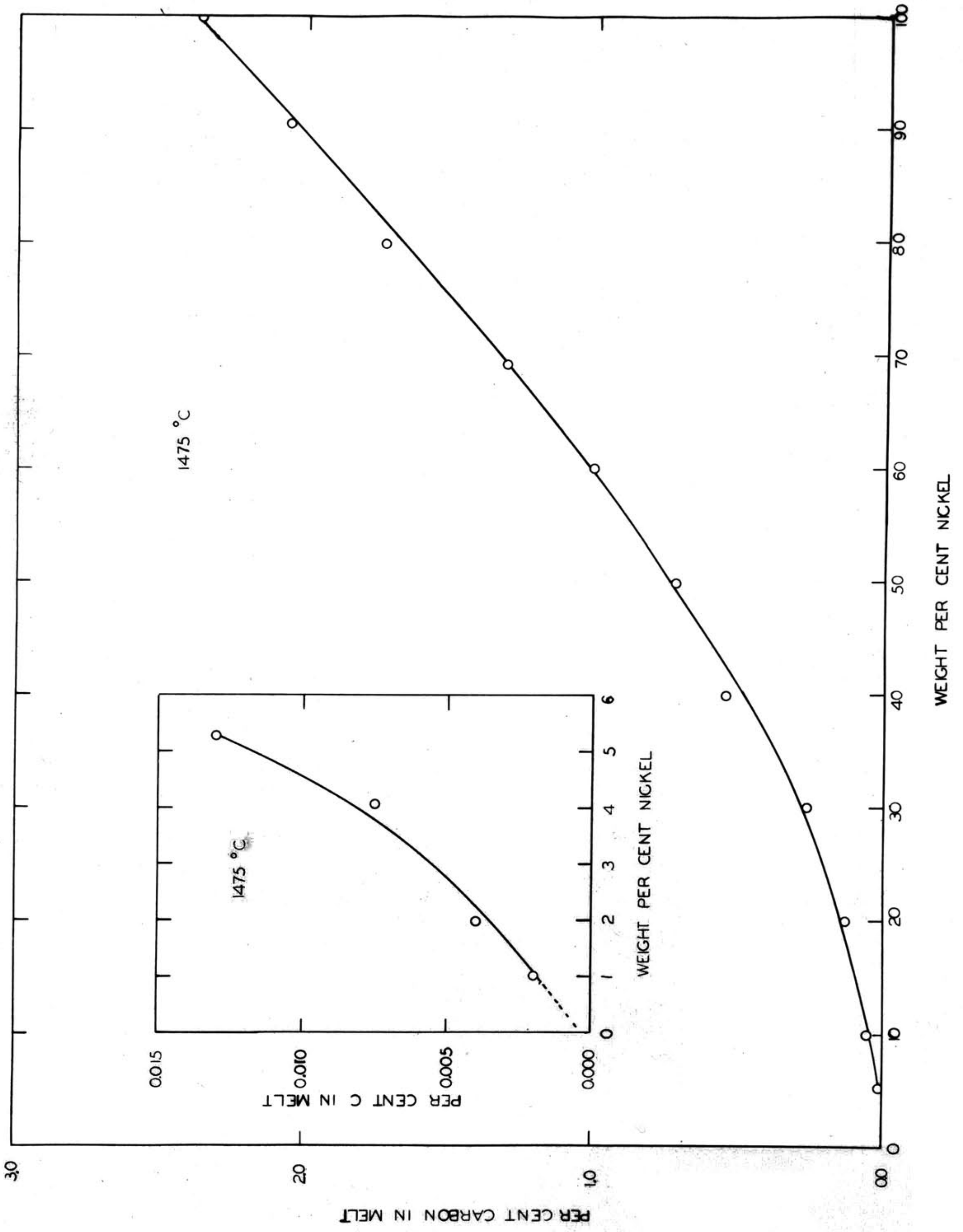


Figure 3. Solubility of Carbon in Molten Copper-Nickel Alloys as a Function of Nickel Content.

TABLE NO. 3

Carbon Content of Quenched Samples of Manganese

Sample Number	Conditions of Saturation		Per Cent Carbon
	Temp. °C	Time Min.	
36	1220	40	6.725
29	1265	30	(6.319)
34	1265	60	6.749
37	1350	40	6.765
35	1400	45	6.808
38	1450	46	6.864

Value in Brackets, ( ), not plotted in Figure 4.

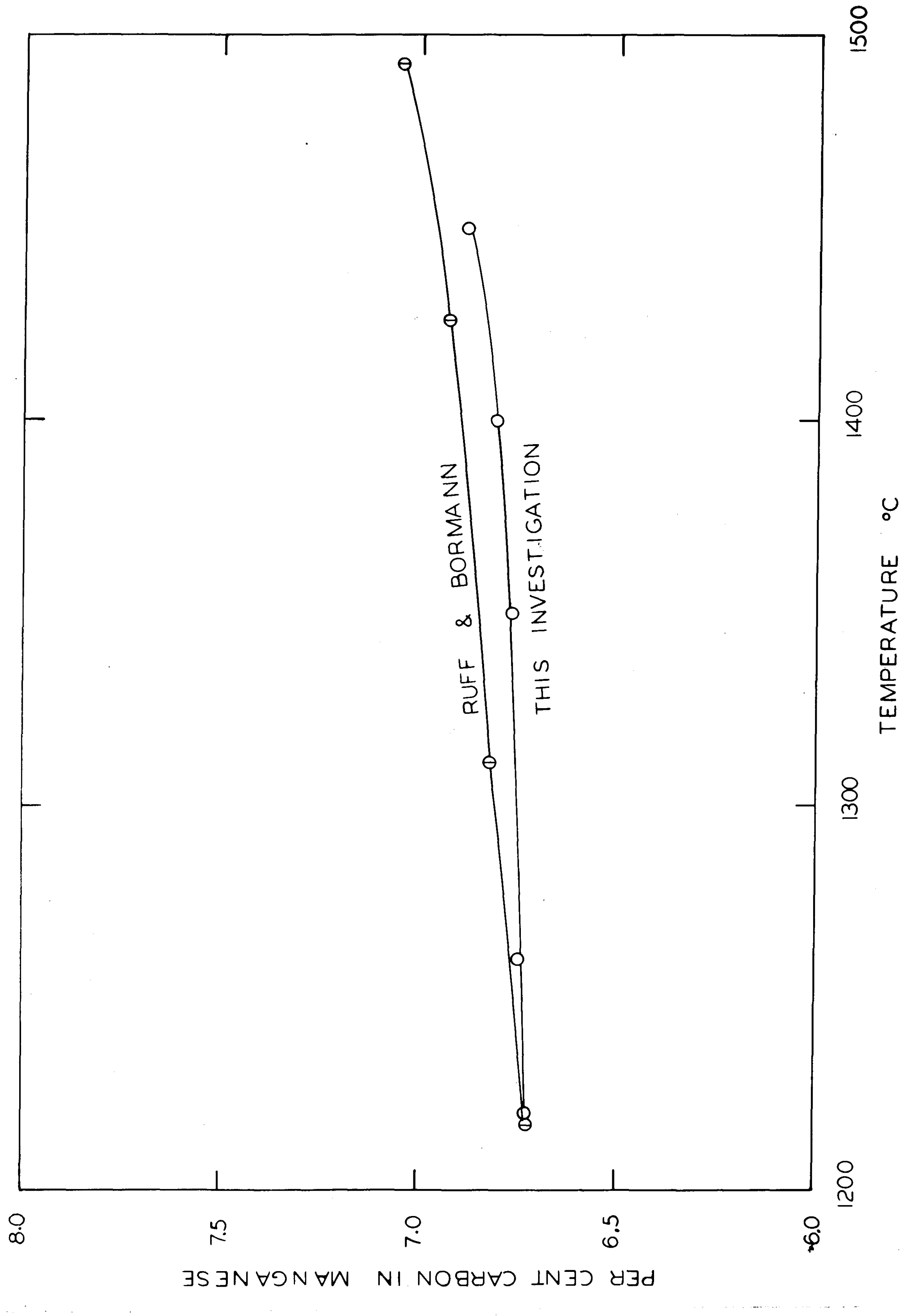


Figure 4. Solubility of Carbon in Molten Manganese as a Function of the Temperature.

IV DISCUSSION OF METHODS AND RESULTS

1. Preparation of Samples

The carbon content of the solidified samples represented equilibrium values only if the following conditions were fulfilled: (1) the liquid bath was saturated with carbon; (2) this saturation amount was retained quantitatively in the sample during quenching; and (3) the sample remained free from mechanically included carbonaceous matter.

The period at which the quenched samples were held at the saturation temperature was long enough to reach equilibrium. To substantiate this, several samples were made by holding them at the saturation temperature for different periods of time. Inspection of the values for samples number 9 and 13, 10 and 12, and 30 and 33 shows that no increase in carbon content occurred in the samples saturated for periods of about 3 times the usual saturation time.

Molten manganese probably dissolves molecular nitrogen. Argon, therefore, was selected as the protective atmosphere for the high-manganese samples. However, the consistency of both sets of results suggests that the nitrogen had little if any effect on the carbon solubility and the carbon analysis.

No direct method was available for checking the effectiveness of the quench as such. However, the values for the solubility of carbon in manganese check very closely with those reported by Ruff and Bormann(6).

Aside from the failure to saturate and quench the melts effectively, negative errors in carbon content could be caused by oxidation of the sample. It is well known that the smallest amount of oxygen will remove carbon from molten copper. In run number 29 the crucible cracked, probably during quenching, and steam is likely to have come in contact with the metal. It will be noticed that the observed carbon content of this sample is appreciably lower than that of the sound sample number 34. None of the samples other than number 29 showed signs of oxidation. It is felt that the use of prepurified nitrogen and pure argon together with the presence of hot graphite in the system eliminated oxidation as a source of error.

From the behavior of the high-manganese alloys it is evident that manganese carbide is unstable. Thomson(18) in an unpublished thesis states that manganese carbide, containing small amounts of iron, disintegrated overnight to a brown powder. In the present investigation the samples were analyzed within four hours after quenching. During much of the intervening period they were stored in closed glass bottles to keep them out of contact with moisture and air. Samples of manganese carbide disintegrated to a brownish powder when allowed to stand in contact with the air for several days. When high-manganese alloys were treated with warm water the characteristic odor of acetylene was observed. When a small drop of water was placed on a sample under the microscope small bubbles of gas were observed. The samples stored in glass bottles however showed no signs of disintegration after several days and re-analysis showed no decrease in their carbon content. At the end of three weeks these samples still gave no indication of disintegration.

Positive errors in carbon contents could have been caused by inclusion of mechanically entrapped graphite. Actually this danger is not great if suitable precautions are taken, because of the high surface tension of the liquid melt, which tends to repel and eject graphite. Furthermore the consistency of the results suggests that the samples were free from mechanically entrapped graphite.

The measurement of temperature was a possible source of error in preparing the samples. Optical pyrometer readings become less reliable the farther removed the observed temperature is from the calibration temperature. Therefore, the inaccuracy of the temperature measurements was probably greatest in preparing the copper-nickel samples which were made at 1475° C. The accuracy of temperature measurement was also affected by the fact that the calibration was made with pure copper, the emissivity of which is not necessarily the same as that of the alloys. This probably led to only a negligible error.

The following correction formula was used for the extrapolation of temperature readings;

$$\frac{1}{S} - \frac{1}{T} = k$$

where S is the true temperature and T the observed temperature in degrees absolute, and k is approximately a constant for moderate temperature ranges.

Analyses were made for the manganese content of samples 3 and 5. The values determined by analysis were equal to the calculated values within the experimental error. Moreover no signs were found of evaporation of the metals used in any of the runs. For these reasons the compositions of the charge could also be considered the analyses of the final alloy.

The nickel used in this investigation was of a lesser degree of purity than the manganese. However, the principal impurity in the nickel was cobalt which in the liquid state dissolves very nearly the same amount of carbon as molten nickel. For this reason the presence of 0.7 per cent cobalt probably had only a negligible effect on the accuracy of the results. The other impurities were present in such small amounts that they need not be considered as possible sources of error.

2. Method of Analysis

The carbon dioxide formed from the combustion of carbon in the sample could be weighed to one-tenth of a milligram. In order to get accurate determinations for the samples containing small percentages of carbon, a sample weight of four times the usual one-half factor weight (4 x 1.3635 = 5.4530 grams) was used. Using this sample weight, one-tenth of a milligram of carbon dioxide corresponded to 0.0005 per cent carbon in the original sample.

The smallest percentage of carbon occurred in the alloy containing 1.0 per cent manganese and amounted to 0.0013 per cent.

This value is so close to the experimental limit of the method that its percentage accuracy is low. However, the observed value is consistent with the body of the data as shown in Figure 2. The values for the rest of the samples are greater than 0.002 per cent with good probability of accuracy.

A U. S. Bureau of Standards sample containing 1.002 per cent carbon was used to test the accuracy of the system at the beginning and after completion of most series of analyses. Occasionally the final standard value was found to be too low. In this case the U-tube was filled with fresh ascarite and the values for the preceeding samples were checked by additional analyses.

Each sample was analyzed until two values that checked within the limits of accuracy of the method were obtained. An average of these values was recorded as the per cent carbon in the sample. The individual values are recorded in the Appendix.

3. Significance of Results

The plotted data in Figure 2 show that the influence of manganese on the solubility of carbon is very small in the alloys containing less than about 25 per cent manganese. In fact, it may be said that the curve falls into three parts. In addition to the low-manganese range there is a transitional zone extending from about 25 per cent to about 75 per cent and above this a nearly straight line connects to the value for 100 per cent manganese. Throughout the entire composition range the carbon solubility is less than that which the mixture rule would indicate. Since the absorption of carbon is caused by the manganese, it is evident that until the manganese concentration exceeds at least 30 per cent the activity of the manganese is depressed when it is dissolved in copper. As a matter of speculation it may be suggested that the pattern of the activity corresponds to the phase diagram which has a minimum at about 35 per cent.(10)

Extrapolation of the curve to zero per cent manganese indicates a carbon solubility in pure copper at 1262° C which is of the same order of magnitude as the value reported by Bever and Floe.(1)

At the present time most of the commercially important copper-manganese alloys are in the low-manganese range where the solubility of carbon is relatively small. However enough carbon is soluble to act as a major cause of gas porosity in castings. For example the equilibrium solubility in 100 grams of copper-manganese alloy containing 1.0 per cent manganese is sufficient to form about 2.33 cubic centimeters of carbon monoxide or dioxide at standard temperature and pressure which at the freezing point of the alloy is about 11.5 cubic centimeters of gas if all of the carbon is oxidized. It is probable that the manganese exerts a retarding effect on the oxidation of the dissolved carbon by tying it up as manganese carbide and possibly also by the formation of manganese oxide.

From the data plotted in Figure 3 it is evident that the effect of nickel on the solubility of carbon in copper-nickel alloys corresponds fairly well to the mixture rule. An extrapolation of the curve to zero per cent nickel indicates a carbon solubility of 0.00035 per cent in pure copper at 1475° C, which is of the same order as the value reported by Bever and Floe.(1)

Commercially important alloys of copper and nickel occur over the entire range of compositions. Any carbon present may have an effect on these alloys in the solid state. Nickel carbide is believed to be unstable resulting in the presence of graphitic carbon.

V MICROSTRUCTURES

Microsections were prepared for several of the carbon saturated copper-manganese alloys in the range from 5 per cent manganese to 82.5 per cent manganese and also one for carbon saturated manganese. These microsections represent the as-quenched conditions without subsequent heat treatment.

The alloys containing 5, 10, 20, and 25 per cent manganese (Figures 5 - 8) exhibited a dendritic structure consisting of a light copper-rich matrix and a dark manganese-rich network. At 33 per cent manganese (Figure 9) a peculiar block-like structure manifests itself. This structure is also shown in the 35 and 37 per cent manganese alloys (Figures 10-12). At 35 per cent manganese irregular shaped dark areas make their appearance. These areas are hard to polish. At 50 per cent manganese (Figure 13) manganese carbide particles seem to be present in the grain boundaries. At 82.5 per cent manganese a pronounced acicular structure (Figure 18) can be seen.

Dean(9),(10)) discusses the block structure at length. It will be noticed that this structure occurs at the approximate composition of the minimum melting alloy.

These remarks on the metallography are admittedly incomplete. Further work including heat treatment will be necessary to obtain a better understanding of the structural changes involved in these alloys.

Microphotographs are included in the Appendix.

VI SUMMARY

The solubility of carbon in molten copper-manganese alloys was found to be proportional to the manganese content. It varies from 0.0013 per cent carbon for an alloy containing 1.0 per cent manganese to 6.75 per cent carbon for pure manganese at the temperature level 1262 - 1265° C.

The solubility of carbon in molten manganese was determined to be 6.72 per cent at 1220° C and 6.86 per cent at 1450° C.

For copper-nickel alloys the carbon solubility ranges from 0.0020 per cent for an alloy containing 1.0 per cent nickel to 2.37 per cent for pure nickel at 1475° C.

The solubility of carbon does not obey the mixture rule in either the copper-manganese or copper-nickel alloys. However the deviation is much more pronounced in the copper-manganese than in the copper-nickel system. Qualitative conclusions may be drawn from this fact as to the nature of these metallic solutions. Manganese up to a certain concentration appears to be bound more closely than nickel to copper as a solvent. The phase diagrams of the two systems support this interpretation.

The fact that carbon is soluble in these alloys has practical significance. Dissolved carbon on subsequent oxidation during cooling and solidification may lead to gas porosity. It may also affect the structure and physical properties of the alloys by its presence as a carbide or as free graphite.

VII SUGGESTIONS FOR FURTHER INVESTIGATIONS

It is recommended that the remainder of the samples be heat treated at various temperatures below the liquidus, and that an effort be made to determine what effect the dissolved carbon has on the structure of the alloys. The physical properties of the various carbon saturated alloys should also be studied.

The solubility of carbon in other molten alloys of copper should be investigated. The carbon solubility in the alloys of the ternary system copper-manganese-nickel would also be of interest.

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IX APPENDIX

Sample Number	Grams Cu	Run No.	Grams Mn	Total Weight	Conditions of Saturation				Per Cent Mn	Per Cent Carbon			
					Temp. °C	Time Min.	KW	Gas					
2	36.08	7	33.80	69.88	1277	30	8.7	N	48.5	0.780	0.756		
3	42.15	7	24.78	66.93	1277	40	8.5	N	37.0	0.416	0.380	0.426	
5	41.67	7	20.50	62.15	1277	30	8.6	N	33.0	0.324	0.326	0.348	
6	40.41	7	4.49	44.49	1277	30	10.6	N	10.0	0.022	0.026	0.018	
7	39.23	7	9.80	49.03	1277	30	10.3	N	20.0	0.074	0.078	0.072	
8	36.89	7	1.94	38.83	1262	35	10.7	N	5.0	0.010	0.008	0.010	0.008
9	36.50	7	6.44	42.94	1262	35	10.5	N	15.0	0.042	0.040		
10	30.11	7	10.04	40.15	1262	35	10.0	N	25.0	0.140	0.142		
11	20.25	7	20.25	40.25	1262	30	8.9	N	50.0	0.846	0.816	0.832	
12	34.65	7	11.55	46.20	1262	90	10.15	N	25.0	0.142	0.142		
13	30.53	6	5.38	35.91	1262	100	10.55	N	15.0	0.038	0.049	0.040	0.038
14	39.73	6	0.81	40.54	1262	30	10.9	N	2.0	0.004	0.0025	0.0030	
15	37.92	6	1.58	39.50	1262	30	10.85	N	4.0	0.006	0.007	0.0065	0.0060
16	28.05	6	12.02	40.07	1262	30	8.5	N	30.0	0.264	0.256	0.270	
17	20.92	6	13.94	34.86	1262	30	8.7	N	40.0	0.534	0.516	0.530	
18	38.93	5	2.05	40.98	1090	30	7.9	N	5.0	0.008	0.0070	0.0075	

Appendix, continued

Sample Number	Grams Cu	Run No.	Grams Mn	Total Weight	Conditions of Saturation				Per Cent Mn	Per Cent Carbon		
					Temp. °C	Time Min.	KW	Gas				
19	36.07	5	4.00	40.07	1090	30	7.6	N	10.0	0.011	0.010	
20	33.92	5	5.99	39.91	1090	30	7.7	N	15.0	0.024	0.026	
21	31.44	5	7.86	38.50	1090	30	7.5	N	20.0	0.034	0.038	
22	40.10	1	0.41	40.51	1262	32	11.0	N	1.0	0.001	0.0015	
23	30.11	5	10.03	40.14	1090	36	7.0	N	25.0	0.054	0.056	
24	36.73	1	12.85	39.58	1090	36	6.2	N	32.5	0.134	0.135	
25	24.75	1	16.50	41.25	1090	40	6.0	NA	40.0	0.286	0.298	0.304
26	20.85	1	20.85	41.70	1090	35	5.5	NA	50.0	0.728	0.624	0.630
27	16.55	1	24.83	41.38	1265	30	6.9	NA	60.0	1.322	1.334	
28	10.20	1	30.61	40.81	1265	30	7.0	A	75.0	2.352	2.364	
29			40.00	40.00	1265	30	6.5	A	100.0	6.256	6.352	6.422
30	26.03	1	14.01	40.04	1265	35	7.0	A	35.0	0.3980	0.3900	
31	7.44	1	35.07	42.51	1265	60	6.3	A	82.5	3.712	3.810	
32	16.54	1	24.80	41.34	1090	30	5.3	A	60.0	1.096	1.090	
33	28.14	1	15.15	43.29	1265	100	7.0	A	35.0	0.3880	0.3900	
34			40.00	40.00	1265	60	6.6	A	100.00	6.732	6.762	
35			40.00	40.00	1400	45	8.8	A	100.0	6.820	6.796	

Appendix, continued

Sample Number	Grams Cu	Run No.	Grams Mn	Total Weight	Conditions of Saturation				Per Cent Mn	Per Cent Carbon			
					Temp. °C	Time Min.	KW	Gas					
36			40.00	40.00	1220	40	6.1	A	100.0	6.70	6.72	6.73	
37			40.00	40.00	1350	40	7.9	A	100.0	6.744	6.760	6.770	
38			40.00	40.00	1450	46	9.5	A	100.0	6.888	6.988		
53	29.18	2	3.24	32.42	1265	30	10.5	N	10.0	0.022	0.024		
54	30.51	2	7.62	38.13	1265	31	10.2	N	20.0	0.070	0.074		
			Grams Ni						Per Cent Ni				
1	49.00	7	16.49	65.49	1331	13		N	25.17				
39	27.51	2	0.28	27.29	1475	31	13.1	N	1.007	0.002	0.002	0.0025	
40	39.34	2	0.80	40.14	1475	31	12.9	N	1.993	0.004	0.004	0.0035	0.0045
41	32.99	2	1.40	34.39	1475	31	12.85	N	4.079	0.007	0.0075	0.008	0.007
42	37.94	2	2.12	40.06	1475	30	12.9	N	5.278	0.012	0.014		
43	31.69	2	3.50	35.19	1475	30	13.2	N	9.940	0.052	0.054		
44	32.10	2	8.02	40.12	1475	30	13.5	N	19.990	0.116	0.114		
45	28.44	2	12.30	40.74	1475	30	13.5	N	30.191	0.260	0.264		
46	16.23	2	24.17	40.40	1475	30	12.9	N	60.123	1.008	1.010		

Appendix, continued

Sample Number	Grams Cu	Run No.	Grams Ni	Total Weight	Conditions of Saturation				Per Cent Ni	Per Cent Carbon	
					Temp. °C	Time Min.	KW	Gas			
47	24.11	2	16.12	40.23	1475	30	12.9	N	40.069	0.546	0.540
48	20.25	2	20.18	40.43	1475	30	12.9	N	49.913	0.726	0.720
49	8.42	2	33.67	42.09	1475	30	10.6	N	79.995	1.728	1.720
50			40.00	40.00	1475	30	10.5	N	100.000	2.368	2.370
51	9.45	2	21.32	30.77	1475	30	10.7	N	69.285	1.310	1.306
52	2.91	2	28.93	31.84	1475	30	10.5	N	90.672	2.062	2.056

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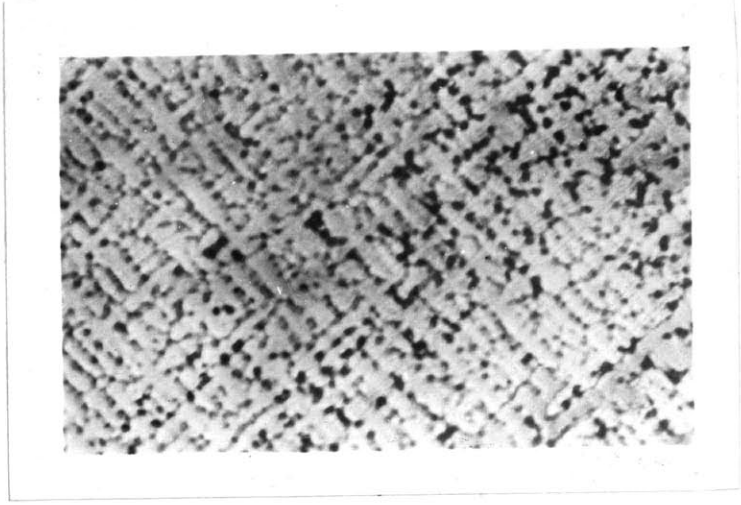

Figure 5. Manganese 5 Per Cent 100X

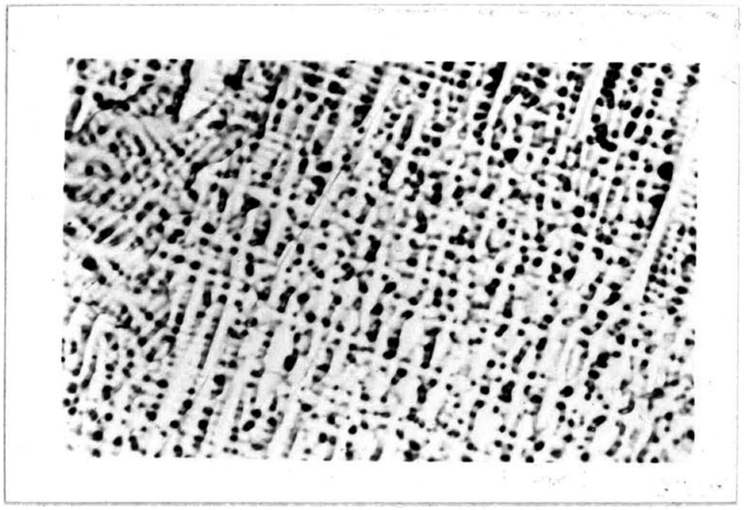

Figure 6. Manganese 10 Per Cent 100X

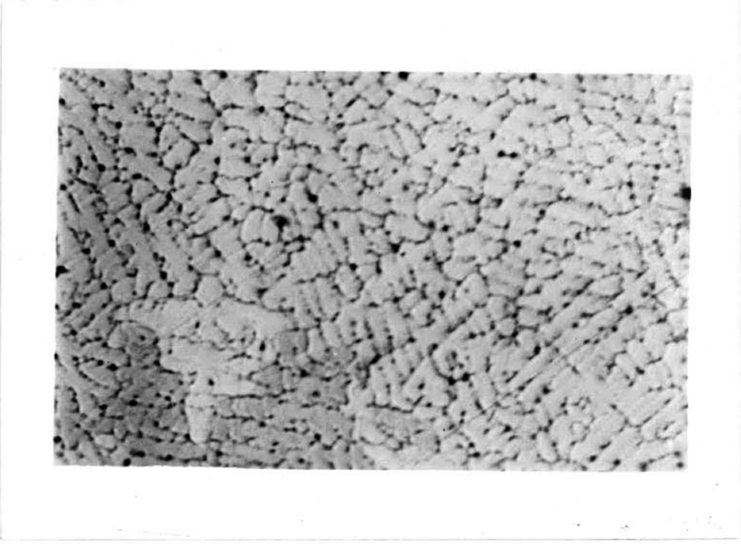

Figure 7. Manganese 20 Per Cent 100X

Figure 8. Manganese 25 Per Cent 100X

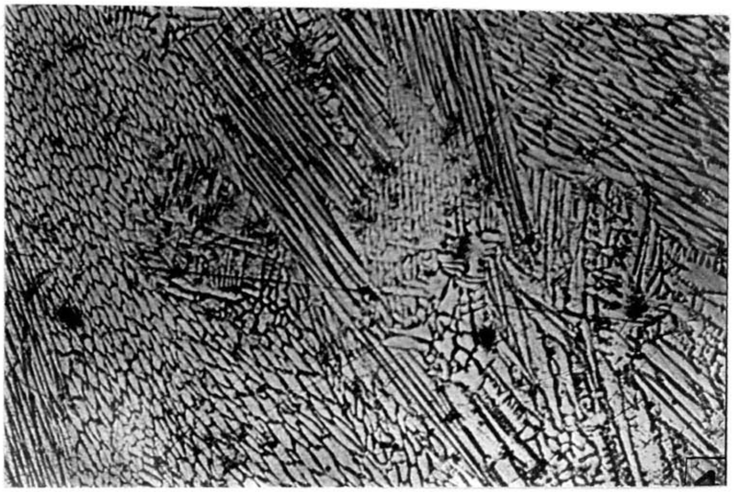

Figure 9. Manganese 33 Per Cent 100X

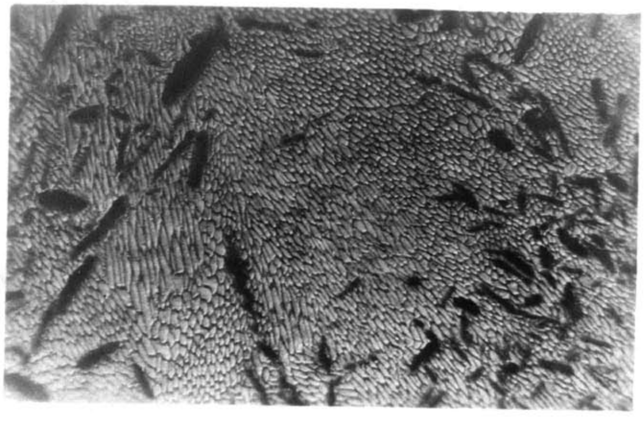

Figure 10. Manganese 35 Per Cent 100X

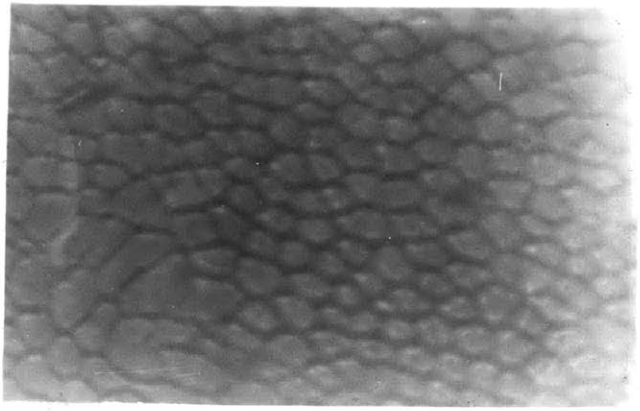

Figure 11. Manganese 35 Per Cent 500X

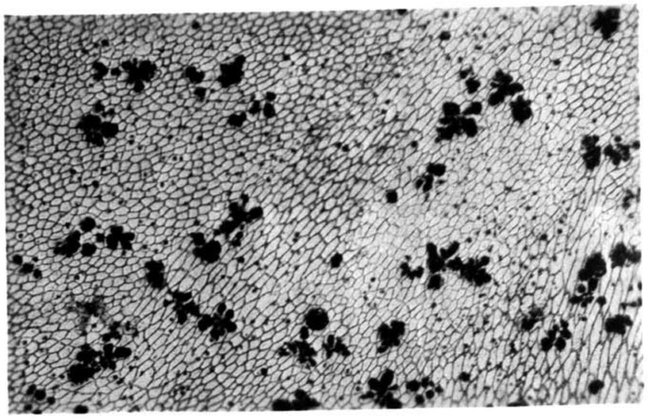

Figure 12. Manganese 37 Per Cent 100X

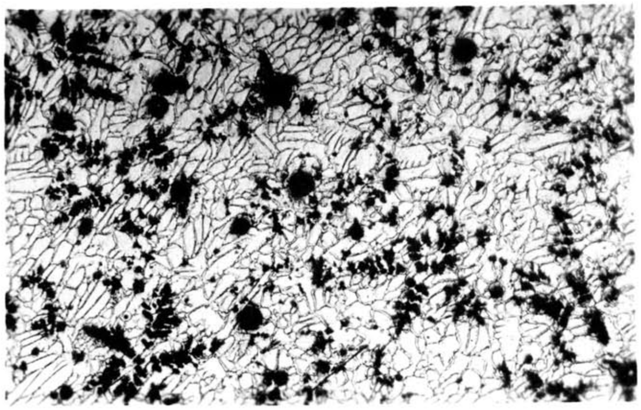

Figure 13. Manganese 50 Per Cent 100X

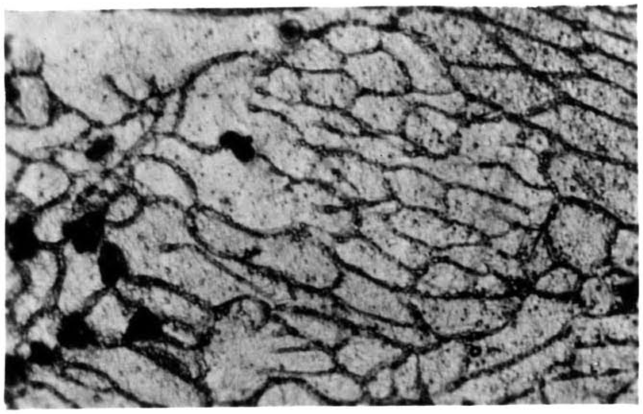

Figure 14. Manganese 50 Per Cent 500X

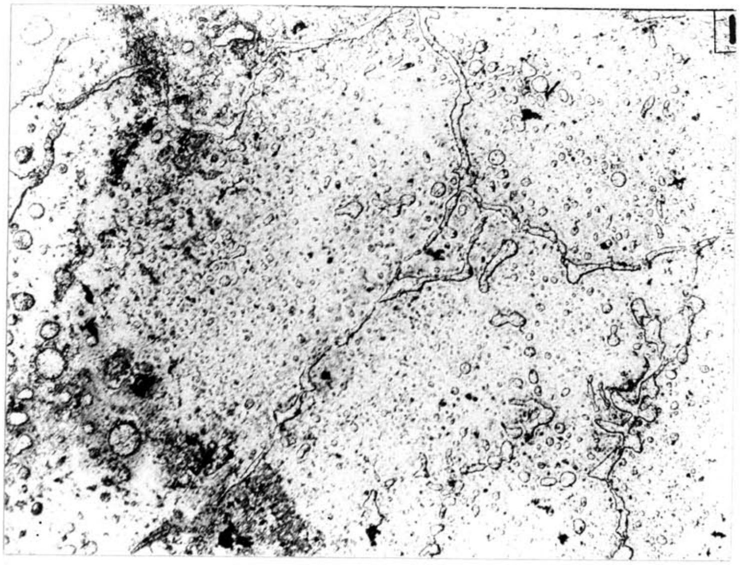

Figure 15. Manganese 75 Per Cent 100X Unetched

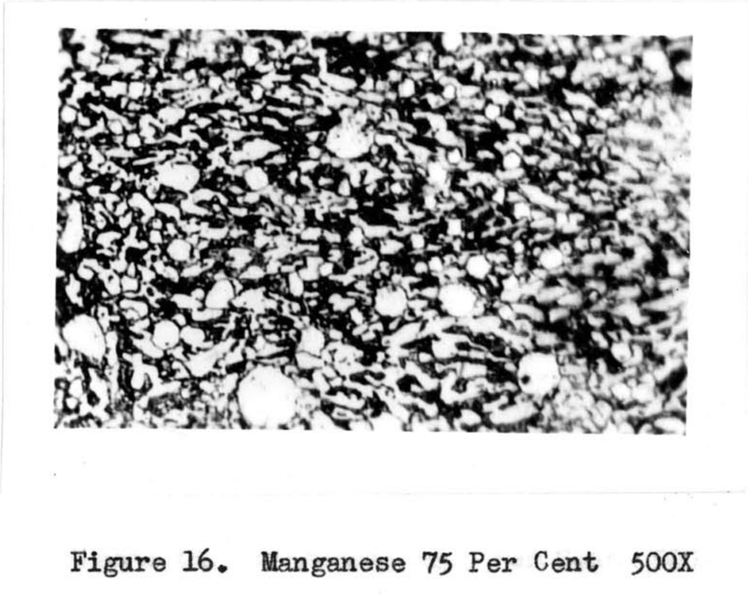

Figure 16. Manganese 75 Per Cent 500X

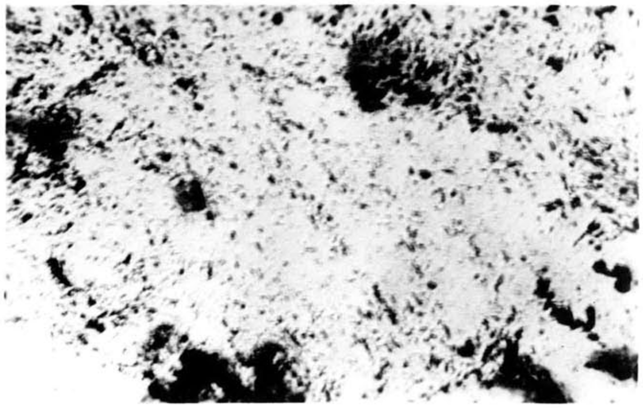

Figure 17. Manganese 82.5 Per Cent 100X Unetched

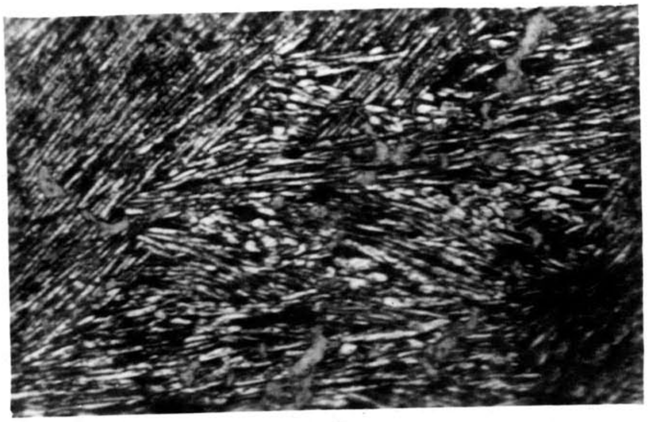

Figure 18. Manganese 82.5 Per Cent 500X

Figure 19. Manganese 100 Per Cent 100X

Figure 20. Manganese 100 Per Cent 500X