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William Alvin Pennington
Iowa State College

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THE DETERMINATION OF THE RATES OF GRAPHITIZATION IN TUNGSTEN-MANGANESE WHITE CAST IRONS

By

W. A. Pennington

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I. INTRODUCTION

Graphitization or malleabilization of white cast iron was discovered quite accidentally by Seth Boyden in Newark, New Jersey, in 1826, while attempting to use Reaumur's method for obtaining white-heart malleable cast iron. The success of his discovery lay in the fact that American pig-iron was low in sulfur and high in manganese content. Since the discovery was not the result of a logical metallurgical development and since much of the work on malleable cast iron was done at a time when analysis of iron was unusual, it can be readily understood that there were many misconceptions as to the proper method of manufacture.

Though the art of making malleable cast iron has developed a great deal since the time of Reaumur and Seth Boyden, there had been very little theoretical work done on this subject before 1920. Since this time, many investigators, especially in Japan and America, have been obtaining results that would lead to a logical explanation of graphitization.

In 1923, Dr. Anson Hayes, Professor of Physical Chemistry at Iowa State College, began a very intensive program to investigate the factors which influence the rate of malleabilization, as well as the properties of the annealed specimens. After the discovery of a shortened annealing cycle, it became evident that, by changing the composition, even a more rapid cycle might be obtained. This work of Dr. Hayes led his successor, Dr. W. H. Jennings, Jr. to begin investigations with alloy cast irons.

The purpose of the investigation reported in this paper was to ascertain the quantitative effects of manganese and various combinations of manganese and tungsten on the decomposition of iron carbide, Fe_3C, in commercial white cast iron.

It was deemed inadvisable to attempt to carry the graphitization through the second stage for the following reasons:
(1) Many hours in the case of a great number of the alloys were required to complete the first stage of graphitization. (2) In general the second stage requires more time than the first.
(3) Manganese because of its effect upon the critical points would necessitate the use of a lower annealing temperature.

A rather careful survey of the literature on the effects of alloying elements in general and the effects of physical factors on the rates of graphitization has been made in order to discuss theory in conformity with the facts herein recorded, as well as those obtained by some other investigators. Some articles, which, without doubt, are extremely important, were not read because of their inaccessibility. Most of these articles are published in journals that have not been located in this country.

II. REVIEW OF THE LITERATURE

A. Constitution of Austenite

Before explaining or understanding the process of graphitization, it is logical that the structure of white cast iron be known. It is conceded that, at a temperature above the A_1 critical point and below the eutectic, it is composed of two phases, namely, cementite and austenite. Cementite generally applies to the iron carbide which appears "free" or in a separate phase. It may also be called "massive" cementite to differentiate it from that cementite which occurs in the eutectoid mixture. The term, cementite, however, has recently been expanded to apply to a single phase which may not only contain iron carbide but other carbides as well. The definitions of cementite are in universal agreement, while those of austenite, at least in some cases, are widely different.

Many authors of text books in metallography define austenite as a solid solution of iron carbide in gamma-iron, while others state that it is either a solid solution of carbon or iron carbide in gamma-iron, and still others regard it as a solid solution of free, atomically dispersed carbon in gamma-iron. According to Bramley and Lord[4] the latter theory is untenable. They state that when an austenitic solution is cooled, for every gram molecule of iron carbide deposited at the Ar_1 point there are 7000 calories of heat evolved in addition to that given out by the iron during its transition from the gamma- to the alpha-state.

On the assumption that austenite is a solution of carbon in gamma-iron, this would represent the heat of formation of iron carbide from its elements, and iron carbide, Fe_3C, would be an exothermic compound. Bramley and Lord, in the above cited article, give a list of investigators, of whom all of the more recent ones have found iron carbide to be endothermic. Consequently, it may be concluded that austenite probably can not be a solution of just carbon in gamma-iron.

Van't Hoff's Law connecting the freezing point of a solvent with the concentration of a solute has been applied by Bramley, according to Bramley and Lord[4], to the depression of the critical points as found in the iron-carbon system. Assuming that austenite is Fe_3C in gamma-iron, he obtained results which are in close agreement with those obtained experimentally, while in making the assumption that austenite is carbon in gamma-iron, the calculated loci are considerably higher. They, therefore, conclude that austenite must contain more iron carbide than carbon.

In their experimental work, they show conclusively that the carbon content of the steel affects the concentration of a $CO-CO_2$ mixture which is in equilibrium with a specific steel at a definite temperature. The following equation may be used in the explanation:

$$CO_2\ (g)\ +\ C\ (g)\ =\ 2\ CO\ (g)$$

Thus if the relative amounts of CO_2 and CO are to shift, the relative amount of carbon in the gaseous form must also change. This change in the amount of gaseous carbon can come only from the steel, since the composition of the mixture remains constant if the steel is absent. It is logical to assume that austenite contains carbon, as well as iron carbide, which exerts a definite pressure at a specific concentration and a definite temperature. Therefore, it follows that there is an equilibrium between the two phases:

$$C \text{ (gas)} = C \text{ (dissolved)}$$

Finally, from the paper of Bramley and Lord, it may be concluded that austenite is a solution of both carbon and iron carbide in gamma-iron.

Jeffries and Archer[24] maintain that it is impossible for molecules of Fe_3C to migrate through the solid solution because of their being larger than the gamma-iron space lattice, and consequently they define austenite as a solution of carbon in gamma-iron. On the other hand, Fry[13] has shown that FeSi and Fe_3P which, in a manner, are similar to Fe_3C as to the size of the molecules, do diffuse in gamma-iron. Accordingly the contention of the former can not be accepted as conclusive evidence as to the constitution of austenite.

Schwartz and co-workers have defined two solid solutions, which are in equilibrium, to explain graphitization. Austenite is regarded as a solution of Fe_3C in gamma-iron. To facilitate the explanation of the process they have postulated the existence of another solid solution in which carbon is dissolved in gamma-iron. To this new solution they have given the name boydenite. The existence of such a solution must necessarily mean that there are three distinct phases in white cast iron in the malleabilization range of temperature, which is contrary to the belief of most investigators who assume only two phases.

Recapitulating, it may be said that the evidence just summarized leads to the acceptance of austenite as a solid solution in which gamma-iron is the solvent and carbon and iron carbide are the solutes.

B. Mechanism of Graphitization

Experimentally, white cast iron of the commercial variety containing two phases in the critical range, namely, austenite and cementite, is converted by prolonged heating into a partially malleable cast iron which, at these temperatures, consists of austenite and temper carbon. Thus, the net result is that the "massive" or "free" cementite phase disappears and a new phase, graphite, appears. This decomposition of the cementite may take place in one of two ways: (1) It may decompose directly. (2) It may dissolve in the austenite from which temper carbon simultaneously precipitates.

In order to accept the former view, it is necessary to establish the fact that Fe_3C, in itself, is unstable at the temperature at which the decomposition takes place. The literature contains many conflicting statements concerning the stability of iron carbide and its heat of formation at temperatures below the solidification range.

Upton[51] takes the view that iron carbide, in itself is not unstable, but that it is metastable in iron-carbon alloys containing impurities, especially silicon. He proposes that the carbon solubility line, when corrected for the effect of silicon, almost if not exactly coincides with the iron carbide solubility line. He quotes Benedicks to the effect that the two systems, iron-carbon and iron-iron carbide coincide at least down to 800°C. Schwartz, Payne and Gorton[44], using an alloy containing 0.05 per cent silicon, about 5.5 per cent carbon, and a few hundredths of a per cent of manganese, phosphorus, and sulfur, found that they could not obtain complete malleabilization. Even after two anneals followed by 400 hours of heat treating near 700°C., 0.9 to 1.0 per cent combined carbon remained. They also suggest that, in the absence of silicon, the eutectoid points of the stable and metastable systems coincide. Evans and Hayes[10], on the other hand, working in this laboratory, have found that Fe_3C, in pure iron-carbon alloys, is metastable at 800 and 927°C. in the presence of CO and CO_2 at a pressure of five atmospheres. Evans and Hayes[10] quote Honda as stating that pure iron-carbon alloys will not graphitize below 900°C. They also report that Schwartz has held a sample at 900°C. for over 2000 hours with no indications of graphitization. Maxwell and Hayes[29], by the calculation of free energy data from equilibrium reactions involving CO and CO_2, have found that Fe_3C is metastable at 650 and 700°C. in practically pure iron-carbon alloys.

These conflicting statements may be accounted for by the fact that the various investigators in no case used absolutely pure iron-carbon alloys. It is, however, rather safe to conclude from the above facts that Fe_3C, in itself is stable even though it may be metastable in pure iron-carbon alloys, and that Fe_3C does not decompose directly in the process of malleabilization or, if it does, it is an extremely slow reaction. Yet, the fact that Chevenard and Portevin[7] accidentally discovered that a steel containing 1.6 per cent carbon, 0.28 per cent silicon and 0.16 per cent manganese may be graphitized at 575°C. by prolonged heating should not be overlooked. This temperature is definitely known to be below the critical range for this type of steel and for this reason Fe_3C may decompose directly. Mellor, in summing up the work of several investigators on the solubility of carbon in iron, states that probably a few hundredths of a per cent carbon dissolve in iron at some temperature very much lower than the eutectoid. So again, the graphitization of the sample of steel by Portevin and Chevenard may have taken place by passing through the solid solution process.

The most prominent theories of graphitization, some of which have been proposed by Kikuta[25], Schwartz[41], Shotton and Hall[46], and Hayes, Diederichs and Dunlap[17] agree in that the Fe_3C, at least in commercial white cast iron, dissolves in the austenite and is subsequently precipitated as temper carbon. This reasoning seems logical when it is realized that many investigators have suggested that the solubility of cementite in gamma-iron is greater than that of carbon. The proponents of the above mentioned theories continue by assuming that, after all of the massive cementite has been dissolved in the solid solution with simultaneous precipitation of carbon, subsequent cooling causes further precipitation of carbon due to its decreased solubility as the temperature decreases. At this point, some of the theories apparently evade the issue and fail to explain exactly what takes place upon abandoning the critical range. Hayes, Diederichs and Dunlap, however, give a rather definite and concise scheme by which the completion of graphitization may take place. According to them, carbon continues to separate on cooling from the maximum annealing temperature until the carbon solubility line (hereafter called Atm line) intersects either the A_3 or the $A_{3,2}$ line. On further cooling, if sufficient time is allowed, ferrite and temper carbon will precipitate simultaneously at the stable eutectoid. With this very slow cooling completely malleabilized cast iron is produced. In case the cooling is a little more rapid, ferrite will precipitate around the carbon spots following the $A_{3,2}$ line until the metastable eutectoid is reached, at which point pearlite will form.

Honda[22] maintains that graphite does not form from the decomposition of iron carbide by the equation,

$$Fe_3C = 3\,Fe + C,$$

but that it forms as a result of a catalytic action of gases, such as carbon monoxide, carbon dioxide, or both. He proposes no definite mechanism, but assumes that carbon dioxide reacts with cementite according to the equation,

$$Fe_3C + CO_2 = 2\,CO + 3\,Fe.$$

The carbon monoxide formed, because of the disappearance of carbon dioxide, as illustrated above, dissociates by the equation,

$$2\,CO = CO_2 + C,$$

to reproduce the dioxide, which again reacts with cementite. Therefore, a small amount of carbon monoxide or carbon dioxide is sufficient to initiate and continue the cycle until all cementite is exhausted.

Honda and Murakami[23] believe that in pure iron-carbon alloys graphitization is caused by the decomposition of the cementite solidified during the process of cooling from the melt. They cite, as evidence, the fact that specimens previously cooled from above 1300°C. did not graphitize by remelting and cooling from any temperature above 1150°C. This fact is explained on the basis that the gases were almost completely expelled during the previous heat treatment. They also found that, when this sample is remelted, the presence or absence of graphite in the specimen does not affect graphitization, which indicates that graphite can not be a product directly separated from the melt.

In explaining the fact that prequenched white cast irons graphitize more readily than the unannealed specimen, Saito and Sawamura[36] advance the view that, due to the great increase in volume in the austenite-martensite transformation, the cementite of the original sample is, in a manner, shattered into smaller particles which present a very much greater surface for reaction.

They state that the graphitization of these fragmental free cementites must mean the direct decomposition of free iron carbide.

From this review, it is evident that, in certain white cast irons, cementite is metastable. Whether it will decompose of its own accord without going through a series of reactions, as may take place in austenite, is still an unsolved problem.

C. General Effects of Alloying Elements on Graphitization

Of the many factors that play an important role in promoting or retarding graphitization, the effect of addition elements is perhaps the most pronounced, with the possible exception of the effect of temperature. The elements, on entering white cast iron, take various molecular forms. It is generally believed that those elements which form carbides more stable than iron carbide tend to delay the decomposition of the latter, while those that form either no carbides or carbides which are less stable than that of iron tend to promote the decomposition.

Henderson[20], from the work of Schwartz and Guiler, reports the following elements as having a positive deleterious effect on the process of malleabilization:

antimony
boron
cerium
chromium
molybdenum
selenium
tellurium
tin

The cerium was impure, having associated with it lanthanum, neodymium, and praseodymium.

On investigating the effect of molybdenum and chromium, Henderson finds that both elements decidedly retard graphitization. He reports that the degree of completion of the second stage is practically negligible for a cast iron containing 5 per cent molybdenum over an interval of 255 hours. Chromium above one per cent is reported as completely stopping graphitization. Likewise, Foulke[12] observed that chromium favors carbide formation, and hence has a pernicious effect on graphitization.

Using the dilatometric method, Sawamura[37] obtained qualitative results which are summarized in the following table:

Table I

Element	Effect on Graphitization
silicon	promotes very strongly
aluminum	promotes strongly
nickel	promotes strongly
copper	promotes moderately
cobalt	promotes slightly
gold	promotes slightly
platinum	promotes slightly
phosphorus	promotes moderately
tungsten	retards slightly
molybdenum	retards slightly
vanadium	retards strongly
manganese	retards very strongly
sulfur	retards very strongly
chromium	retards very strongly

Many of the above results have been checked quantitatively in this laboratory. The work of Henderson and Foulke have already been referred to. In addition, Lykken[28], working with copper alloys, and Lett[26], working with cobalt, find that each of these elements slightly promotes graphitization. The writer has confirmed the results of Table I. pertaining to tungsten and manganese.

In his discussion of the effect of silicon, Sawamura points out that the beginning and end temperatures of graphitization descend rapidly at first, and then more slowly as the silicon content is increased. Carbon has a similar but hardly as pronounced effect as silicon in lowering the beginning temperature.

Aluminum has a favorable effect which reaches a maximum in white cast iron containing 3.45 per cent carbon at 0.5 per cent, and in iron containing 1.8 per cent carbon at 1.5 per cent. On further increasing the percentage of this element little effect is obtained. When the aluminum content is increased to 3 per cent a carbon containing constituent begins to form and increases in amount as the element is added until eight per cent aluminum is reached. At this point, the cementite, which decreases in amount as the other carbon containing constituent increases, disappears completely in the alloys as cast. Thus, since the carbon containing constituent is stable, even at very high temperatures, and since no cementite is present, it is impossible to graphitize a sample containing this amount of aluminum.

Sawamura points out that the type of crystal lattice of the alloying element may have much to do with the effect that is produced. Aluminum, nickel, cobalt, copper, gold, and platinum are face-centered and favor graphitization. On the other hand, chromium, vanadium, tungsten, and molybdenum, which have a body-centered lattice, have an unfavorable effect.

In regard to the effect of cobalt, the literature seems to be somewhat contradictory. While Sawamura[39] and Lett[26] find that cobalt has a favorable influence, R. C. Good[14] states that it promotes the formation of carbides. Bauer and Piwowarsky[2] support the view of Good in believing that cobalt tends to prevent the precipitation of graphite, and consequently aids in the formation of carbides.

Schwartz[41] finds that silicon, nickel, aluminum, titanium, zirconium, and uranium have a favorable effect upon graphitization, while chromium, manganese, sulfur, antimony, selenium, and tellurium distinctly interfere with the process. He states that tin, and cerium including the rare earths may hinder graphitization. He lists columbium, platinum, tungsten, gallium, palladium, and tantalum as elements which have no measurable effects. His result concerning tungsten certainly is not in agreement with that obtained by Sawamura nor that obtained by the writer who finds that tungsten, though the effect is slight, does retard graphitization .

The quantitative effects of silicon, carbon, manganese, sulfur, and phosphorus have been determined by Kikuta[25]. According to his data, silicon has a very strong promoting effect upon both the first and second stages of graphitization; carbon has a greater effect on the second stage than silicon, although it hardly affects the first stage; sulfur has a retarding effect upon both stages, though the effect on the second stage is more outstanding; phosphorus assists graphitization in the first stage, but its content should not exceed 0.6 per cent if the process is to be carried through the second stage. Kikuta's work on manganese will be discussed in detail later in this paper.

The writer has made no attempt to review all of the literature concerning the effects of the various elements, but is merely reporting some information, which may facilitate theorizing in a latter portion of this paper, that was incidentally found while searching for data on the effects produced by manganese and tungsten.

D. Influence of Various Gases and Packing Mediums on the Rates of Graphitization

The investigation of the effects of various gases on the rates of graphitization of white cast iron has just recently attracted attention. The effects of such gases as carbon monoxide and carbon dioxide, however, have been observed by different experimenters for the past decade. Some theories of graphitization depend on the assumption that these two gases act as carbon carriers. Such assumption would naturally lead to the investigation of their influence, as well as the influence of other gases. Hayes and Scott[19] showed that graphitization was accelerated in the presence of a carbon monoxide-carbon dioxide mixture under increased pressure.

The effect of oxygen presents a rather peculiar problem. It causes graphitization to proceed with an increased readiness, according to Honda and Murakami[23], when it is previously introduced into the molten metal in the gaseous form. It has been shown, however, by Matsubara[30] by a study of gas equilibria that Fe_3C is more easily prepared from Fe_2O_3 than from Fe. He also demonstrated that Fe_3C is stable toward carbon in an oxide bearing metal and hence, obviously, stable toward itself. This apparent contradiction may be explained by the assumption, that in the former case the oxygen is present as a gas and furnishes a medium for the migration of carbon in the form of carbon monoxide or carbon dioxide, and that in the latter case the Fe_2O_3 is present in the solid phase and shifts the equilibrium diagram in such a manner that Fe_3C is more stable.

The effects of several gases on the graphitization of a cast iron containing 2.48 per cent carbon, 1.02 per cent silicon and 0.19 per cent manganese has been reported by Sawamura[39]. A table of his data follows:

Table II

Gas	Tempt.	Time (hours)	Carbon loss
vacuo	975°C.	1.5	0
hydrogen	975°C.	10 + x	0.31%
ammonia	975°C.	10 + x	0.19%
methane	975°C.	10 + x	0.16%
nitrogen	975°C.	1.83	very little
oxygen	975°C.	2 +	- - - -
carbon monoxide	975°C.	3.16	- - - -
carbon dioxide	975°C.	1.5	0.44%
air	975°C.	1.83	0.42%

Water vapor interferes slightly when it is in an atmosphere of nitrogen. No explanation for the effects of gases was revealed in the above mentioned article. There is a previous article[40], which was inaccessible, in which Sawamura may have discussed the theory connected with the effects of various gases.

In regard to the effect of packing materials upon graphitization Sawamura reports that, (1) the process takes place faster when the specimen is packed in various iron oxides and oxides of other metals than when packed in silica sand, (2) roll mill scale has an acceleration over silica sand, and (3) various carbonates, such as barium carbonate and dolemite, have an accelerating influence.

E. Some Physical Factors which Affect Graphitization

a. Annealing Temperature

Reference has already been made to the fact that temperature is one of the most important factors to be considered in graphitization of white cast iron. Increasing temperature has a very marked favorable effect. Kikuta[25] gives the following data in support of this fact.

Table III

	C(%)	Si(%)	Mn(%)	S(%)	P(%)
Analysis of sample	2.28	1.02	0.31	0.034	0.126
Annealing temperature	870°C.		905°C.		905°C. ✗
Time required for the completion of the first stage of graphitization	9 hrs.		4.5 hrs.		2.5 hrs.

Thus, it is seen that raising the temperature 35°C. just about doubles the speed with which the graphitization proceeds. These data show that, in order to have consistent and comparable results, the temperature at which graphitization takes place must be accurately known. This factor may account for the fact that the results of some investigators appear anomolous.

b. Tapping Temperature

Honda and Murakami[23], in a series of fifteen experiments, showed that the higher the tapping temperature the longer was the time necessary for graphitization. They explained this phenomenon on the basis that the solubility of the carbon-carrying gases, carbon monoxide and carbon dioxide, diminished with increasing temperature until finally they were practically insoluble. No graphitization took place in a sample that had been heated at 1300°C. for ten minutes. Kikuta's explanation of the effect of temperature agrees with that of the former mentioned investigators. A table of his data, which shows the quantitative effect of the tapping temperature follows:

Table IV

	C(%)	Si(%)	Mn(%)	S(%)	P(%)	
Analysis	2.70	0.98	0.30	0.018	0.111	
Tapping temperature (°C)	1300	1350	1400	1450	1500	1550
Time (hours) required to complete the first stage at 925°C.	5	5.5	6.33	7	8	8.33

c. Rate of Cooling of Casting

It is generally know that the rate of graphitization at constant temperature varies directly as the rate of cooling of the casting previous to annealing. Many investigations, a greater part of which have been qualitative, have been made on the effect of this factor. Notably among the quantitative investigators are Schwartz, Johnson and Junge[43]; Saito and Sawamura[36]; and Kikuta[25]. Some of the data of Kikuta are reproduced in Table V and some of that of Saito and Sawamura in Table VI.

Table V

No. of specimen	C(%)	Si(%)	Mn(%)	S(%)	P(%)	
5	2.47	1.07	0.30	0.018	0.117	
6	2.56	0.99	0.19	0.028	0.137	
Temperature of mould (°C)	Green sand	Dry sand	400	600	800	1000
Time (hrs.) for complete graphitization at 925°C. No.5	5	6	7.5	9	9.33	10
No.6	-	8	-	11.33		15.33

Table VI

Composition C(%)	Si(%)	Time (hours) to complete first stage at 950°C: as cast	quenched from 850°C. in water (24°C.)
2.40	0.70	13	3 1/3
	0.80	11	2 2/3
	1.00	6	1 1/2
	1.30	3 1/6	2/3

Schwartz, Johnson and Junge[43] found that cast iron which had been prequenched from 800°C. graphitizes so quickly that it is almost impossible to determine the time necessary for its completion. It is obvious that this difficulty of measuring the time is due to the inadequacy of the microscopic method for measuring the time for graphitization when that time is very short. The dilatometric method is certainly to be recommended for sampleswhich malleabilize so rapidly. The above investigators state that they obtained data which so closely agreed with that of Sawamura that they did not publish it.

Prequenched white cast iron, after being graphitized shows smaller nodules of carbon than those found in the normally cooled specimens. This phenomenon is, with little doubt, due to the refinement of the grain structure on quenching.

F. Cast Iron Containing Manganese

A search of the literature reveals that many contributions have been made concerning the effect of manganese on the graphitization of white cast iron. Much of this work has been of a qualitative nature. The quantitative data which have been obtained were for specimens containing relatively low percentages of manganese. No complete investigation has been made with a cast iron containing more than 2.11 per cent manganese.

The researches which have been done with these lower percentages of manganese reveal that manganese not only affects the rate of decomposition of the iron carbide, Fe_3C, but it also has a destructive effect on any iron sulfide, FeS, that may be present, converting it to manganese sulfide, MnS. As shown by Hoelscher[21], iron sulfide has an extremely marked deleterious influence on the rate of graphitization, while manganese sulfide appears to have little or no effect. The difference in the effects of the two compounds may be explained on the basis of the difference in their melting points. Levy[27] believes that iron sulfide forms films which envelop the grains of cementite, and consequently, because of their opposition to the expansion that accompanies graphitization, they retard the process. Manganese sulfide, on the other hand, forms little globules which are embedded in the matrix, and therefore have but little effect on the process. From the foregoing citations, it is obvious that, in correlating the available data, the effect of manganese on the rate of decomposition of iron carbide can not be predicted unless iron sulfide be practically absent or its effect duly considered.

Since manganese, when present as manganese carbide, retards graphitization very notedly and since manganese sulfide has little effect, the addition of a definite amount of sulfur will correct for the effect of manganese. Conversely, manganese may be added to correct for the harmful effect produced by sulfur when in the form of FeS. Evidantly there must be some optimum ratio of manganese to sulfur. Hoelscher found that this ratio should be 4.6 for cast iron containing 2.10 per cent carbon and 5.4 for that containing 2.40 per cent carbon. Hoelscher quotes Gilmore as stating that the Mn/S should never be below 1.7 if good malleable iron is to be obtained. Yemenidijian[53] states that, "the optimum percentage of manganese to balance the effect of sulfur in retarding graphitization is about twice the per cent of sulfur plus 0.15 per cent manganese. This value is lower for high silicon alloys". The highest percentage of manganese in any of the alloys that Yemenidijian used was 0.66, while the maximum in those of Hoelscher was 0.397.

On the assumption that there is enough manganese to balance the effect of the sulfur, any additional manganese will react with iron carbide by the equation,

$$Fe_3C + 3\ Mn = Mn_3C + 3\ Fe.$$

The manganese carbide thus formed will remain in solid solution with the iron carbide. This cementite is by no ordinary means distinguishable from Fe_3C cementite. Manganese, in pure iron-carbon alloys, tends to increase the stability of cementite, lowers the temperature of primary solidification and lowers the eutectic temperature slightly[9]. Guillet[16] states that manganese forms a double carbide which prevents graphitization. Manganese-iron-carbon alloys containing more than 0.8 per cent manganese are very brittle. Osann[33] says that this defect can be removed by very slow cooling. In investigating the manganese-carbon system, Stadeler[47] found that manganese would absorb 3.6 per cent carbon at 1450°C. in one hour and 6.72 per cent at 2000°C. in the same length of time. He verified the belief that Mn_3C is brittle by immersing the hot alloys in water. Those which contained more than three per cent carbon immediately fell to pieces.

According to a curve, constructed or reproduced from the data of Sawamura by Coyle[8], manganese, as well as carbide forming elements in general, raises the temperature of beginning graphitization. From this curve it may be noted that when the manganese content exceeds 2.5 per cent the temperature of beginning graphitization exceeds 1800°F. The writer had no unusual difficulty in completely decomposing the free cementite in a cast iron containing 5 per cent manganese at 1700°F. This apparent conflict may be explained by the fact that Sawamura progressively increased the temperature while the writer experimented at a constant temperature.

The effect of manganese in retarding graphitization in the first stage is well shown by the following data of Kikuta[25]:

Table VII

No. Specimen	C(%)	Si(%)	Mn(%)	S(%)	P(%)	Time for first stage at 925°C
47	2.62	1.15	0.22	0.026	0.126	5 hrs.
40	2.51	1.15	0.46	0.033	0.127	5 1/2 hrs.
41	2.61	1.20	1.02	0.033	0.130	7 hrs.
42	2.64	1.12	1.26	0.024	0.136	8 hrs.
43	2.64	1.15	1.81	0.013	0.134	13 hrs.
44	2.72	1.15	2.11	0.022	0.129	22 hrs.
45	2.66	1.11	3.16	0.013	0.133	25 + X

Sample No. 45 suffered no graphitization after being heated for 25 hours at 925°C.

Hayes and Flanders[18] found that manganese is much more effective at low than at high temperatures.

G. Cast Iron Containing Tungsten

The effect of tungsten upon graphitization in white cast iron has not been so carefully pursued as has the effect of manganese. A survey of the literature has revealed nothing more than qualitative data which are very much in disagreement.

Coyle[8] classes tungsten, along with nickel, aluminum, titanium, and copper, as graphitizing elements stating that, "These elements cause cementite to decompose into graphite and pearlite and possibly some ferrite". Schwartz[41] lists tungsten with columbium, platinum, gallium, palladium and tantalum as elements which have no measurable effect. In contradiction to these two views, Sawamura proposes that tungsten retards graphitization although the effect is slight.

The system involving tungsten may be expected to be more complicated than that of manganese because it contains many more molecular species. According to Persoz[34], tungsten goes into cementite forming a very stable complex carbide with iron. Sisco[45] states that tungsten reacts with both iron and carbon to form complexes whose general formula may be represented as $xFe_3C.yWC$. He concludes that it is rather certain that WC exists in tungsten cast iron, and that there are also probably such compounds as Fe_2W and Fe_3W present. In working with the tungsten-carbon system, Becker[3] concluded that WC forms and is stable up to

1900°C. at which temperature it decomposes into W_2C and C.

Using the dilatometric and magnetic methods, Takeda[48] has determined the equilibrium diagram of the tungsten-carbon -iron system. He finds that, in this system, there are two equilibrium diagrams. The Fe-C-WC is the stable system, while the Fe-θ-η system is metastable. The θ -phase is a ternary solid solution composed chiefly of Fe_3C which decomposes on annealing to graphite and iron. The η -phase is also a ternary solid solution consisting mainly of a double carbide, Fe_3W_3C, which decomposes into WC and Fe. The excess tungsten probably unites with carbon from the θ-phase to form more WC.

Due to the great complexity of the tungsten-iron-carbon system, to say nothing of the complexity of the tungsten-iron-carbon-manganese-silicon system, it is difficult to predict the effect that would be produced upon the stability of Fe_3C when tungsten is introduced into cast iron.

III. INTERPRETATIONS AND THEORETICAL CONSIDERATIONS

In the main, the writer agrees with Kikuta, Hayes and co-workers, Schwartz and co-workers, and Shatton and Hall on their views on graphitization. At this point, however, a more detailed mechanism will be proposed.

Graphitization,at constant temperature in the critical range may be assumed to take place by either or both of the following equations.

(1) $Fe_3C \rightleftharpoons 3\ Fe + C$

(2) * $Fe_3C + CO_2 \rightleftharpoons 3\ Fe + 2\ CO$

Since it is believed that Fe_3C, in itself is stable, reaction (1) apparently will not take place in the cementite unless it is contaminated with some impurity such as silicon. The application of this equation may be shown from the assumption that austenite is a solid solution in which both carbon and iron carbide are dissolved. From this assumption, it follows that there is probably an equilibrium in this solid solution between iron, carbon, and iron carbide, as shown by equation (1) and too, since the austenite is saturated with respect to iron carbide, there must be an equilibrium between the dissolved iron carbide and that which occurs as cementite. Consequently, upon heating a sample of white cast iron to 925°C., some such condition, as represented by equation (3), must exist:

(3) $Fe_3C\ (\text{undissolved}) \rightleftharpoons Fe_3C\ (\text{dissolved}) \rightleftharpoons 3\ Fe + \underset{(\text{dissolved})}{C}$

After the specimen begins to undergo malleabilization, a new phase, temper carbon, appears and another equilibrium is added, to those above:

(4) C (dissolved) $\rightleftharpoons$ C (temper carbon)

From probability, it is known that an absolutely true equilibrium does not exist, but instead the reacting molecules behave in such a manner that the equation vibrates, so to speak, about some mean position. Of course the larger the number of molecules the more nearly perfect is the equilibrium. Let us consider that the equilibria represented by equations (3) and (4) are for just an instant, disturbed toward the right and that more Fe_3C has dissolved than is required to saturate the solution. The dissolved iron carbide or an equivalent amount of iron carbide may either immediately precipitate or it may even further disturb the equilibrium, in the same direction, by reacting to give ferrite and dissolved carbon. If the former took place, the equilibrium would be restored; while if the latter took place iron and carbon would be forced to react to give dissolved Fe_3C which, in turn, could precipitate to restore the equilibrium. Moreover, since the solution is at some time supersaturated with respect to carbon, it is reasonable to expect this excess carbon, at least in a certain fraction of the total chances, to precipitate as temper carbon. If the equilibria are disturbed to this extent, at a particular instant, it follows that they can be reestablished in two ways: (1) The carbon can redissolve, reunite with iron to form iron carbide which is in solution and then precipitate as iron carbide of the cementite. (2) More iron carbide can dissolve from the cementite and dissociate to such an extent as is required by the equilibria. In the former case, the net result is that no reaction has taken place, but in the latter case, it is obvious that temper carbon has been formed at the expense of solid iron carbide. On the other hand, it is just as logical to make a similar assumption that the equilibria be disturbed toward the left. With such an assumption, it may be seen that solid iron carbide may be formed from temper carbon if it is present. The net result of the above shifting of equilibria depends on the relative solubility of carbon in the form of carbon and in the form of Fe_3C. Fig. 1 shows an Fe-C equilibrium diagram determined by Hayes in which the silicon content was held constant at about one per cent. From the diagram, it may be noted that carbon is considerably less soluble from carbon than from iron carbide when silicon is present. Therefore, whenever the carbon is precipitated, its chance of redissolving to restore the equilibria is less than the chance that the restoration will come about by solution of iron carbide. Since this is true, it is manifest that, if time is allowed, all of the cementite will decompose producing partially malleabilized cast iron, and that temper carbon will not produce cementite at a constant temperature operation.

The above proposed mechanism, as previously stated, depends on the relative solubility of carbon and iron carbide. From the review of the literature and from data which have been obtained by the writer using manganese alloy cast irons, it is probably true that the Atm and Acm lines coincide in pure iron-

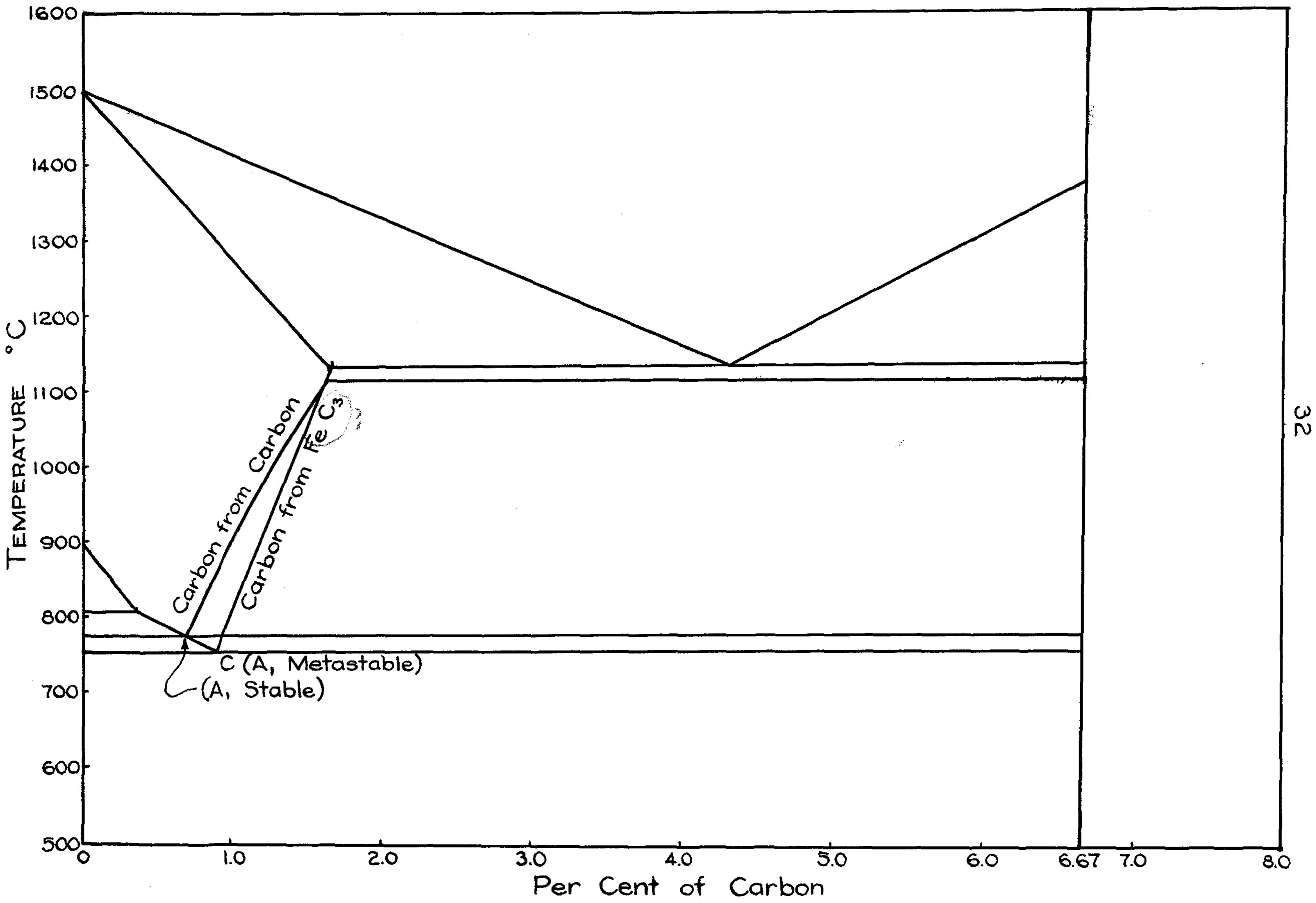

FIG. 1 IRON-CARBON STABLE AND METASTABLE SYSTEMS

carbon alloys. In such a case, it would be impossible to have graphitization, because the chance of dissolving carbon would be equal to the chance of dissolving iron carbide. Apparently, in order to have graphitization, the chance of dissolving carbon must be much less because graphitization, even in the mild silicon alloys, does not proceed readily until the solid carbon phase is present. In other words, if the Atm and Acm lines coincide, the excess carbon, which may be present for a particular instant, merely serves to supersaturate the solution. This supersaturation is not relieved by precipitation, but by a reversal of equation (3).

It is an accepted fact that silicon causes a remarkable difference in the solubility of carbon and iron carbide. Diagrams for the Fe-Si-C system have been presented by Sato[37] in which he bears out the former statement. Since silicon decreases the solubility of carbon, while, at the same time, having but little effect on the solubility of iron carbide, the above mechanism with some alterations to duly consider the silicon is entirely adequate. The silicon when introduced and perhaps later is in the form of FeSi. It is conceivable that this compound may react with Fe_3C which is in the dissolved form,

(5) $FeSi + Fe_3C = 4\,Fe + SiC = 4\,Fe + Si + C$

The carbon thus formed aids in supersaturating the solution and in so doing causes the carbon to precipitate faster. The silicon probably reacts with more iron to form the silicide. The speed of graphitization in silicon cast iron, therefore, depends upon the speed with which this cycle is completed. The fact that SiC is unstable is supported by Enos[9].

It is not advisable to put so much stress on reaction (1) that reaction (2) will be forgotten. In all probability it also plays an important role. Like reaction (1), it may be thought of as taking place at the surface of the cementite or, in the austenite. If carbon dioxide reacts directly with Fe_3C of the cementite phase, the mechanism is rather simple; if it reacts in the solid solution, several equilibria must be considered. For instance the carbon monoxide formed will tend to form more carbon dioxide according to the equation,

$$(6) \quad 2\,CO = CO_2 + C$$

When it is recalled that carbon is formed by two different methods - first by reaction (1); second by reaction (2) and (6) - it is evident that there exist three equilibrium constants for this particular phase:

$$\text{Reaction (1)} \qquad K_1 = \frac{a^3_{Fe}\, a_C}{a_{Fe_3C}}$$

$$\text{Reaction (2)} \qquad K_2 = \frac{a^3_{Fe}\, a^2_{CO}}{a_{Fe_3C}\, a_{CO_2}}$$

$$\text{Reaction (6)} \qquad K_6 = \frac{a_{Fe_3C}\, a_C}{a^2_{CO}}$$

Since the values of any particular K must remain constant and since each activity appears in two constants, it is seen that the three reactions are interdependent. The formation of carbon by reaction (1) tends to oppose reaction (6). And further, the reversal of reaction (6) tends to oppose reaction (2). Likewise the formation of carbon by reactions (2) and (6) tends to oppose the formation of carbon by reaction (1). As soon as the excess carbon precipitates from the solid solution, either of the above reactions may take place unhindered. The carbon dioxide formed by reaction (6) may again react with iron carbide and thus continue the cycle. This possibility is the basis for thinking that a little carbon dioxide is necessary for obtaining optimum graphitization.

The mechanism, thus far presented, does not explain the fact that cast irons, in which all of the original free cementite has been converted to iron and temper carbon, continues to graphitize below the austenitic region when cooled slowly from the maximum annealing temperature and held slightly below the eutectoid. Neither does it explain the fact that steels will graphitize at 575°C. as shown by Chevenard and Portevin[7].

When a sample of cast iron, which has been completely graphitized through the first stage, is cooled slowly from the maximum annealing temperature, carbon continues to separate from the solution as represented by the carbon solubility line in Fig. 1. This separation continues until the stable eutectoid is reached at which iron and carbon will precipitate simultaneously. Between the stable and metastable eutectoids iron and carbon continue to precipitate together, but more iron is precipitated than that required at the stable eutectoid, as represented by the line BC of the diagram. At C most of the solid solution is converted into a mixture of ferrite and cementite known as pearlite. Some of the solid solution is converted into another solid solution differing from the first as to the concentration of the solutes and as to the form of iron (gamma-iron in the former; alpha-iron in the latter). Here again the process of malleabilization may continue in a similar manner to that which took place in the critical range. When alpha-iron is present the process is considerably slower for two reasons. (1) The temperature must be lower for the existence of alpha-iron. (2) The difference in solubility of carbon and iron carbide are probably not so pronounced. It is the writer's contention that if these solutions in alpha iron did not exist it would be impossible to achieve graphitization in the second stage.

Since the existence of the solutions in alpha iron seem to be so important some evidence in favor of their existence will be presented. From the fact that delta-iron is known to dissolve carbon and from the fact that delta-iron and alpha-iron are both body centered, S. Tamura[49] reasoned that alpha-iron would dissolve carbon. He drew a line, in the iron-carbon diagram, from the point of maximum solubility of carbon in delta-iron at about 1484°C. to about .034 per cent carbon at room temperature assuming that points on this line would represent the solubility of carbon in alpha-iron at the various temperatures, provided alpha-iron existed at the temperature in question. He proposes that the solubility of carbon in alpha-iron would be the same as that in delta-iron at a specific temperature, if they were co-existent.

As has been intimated, he had previously accepted .034 per cent as the solubility at room temperature. Sauveur and Kirvobok[38] state that, "alpha-iron is capable, after slow cooling, of retaining in solution at least .06 per cent of carbon". Yensen[54] working with the magnetic properties of Fe-C and Fe-Si-C alloys, concluded that carbon is soluble in alpha-iron up to probably .02 percent. He quotes N. B. Pilling to the effect that carbon is soluble up to .005 per cent.

These conclusions certainly seem to be sufficient to justify the use of shifting equilibria-mechanism for an adequate explanation of graphitization in both the first and second stages.

Having discussed the effect of silicon in conformity with the above theory it may be interesting to note how the effects of some of the other elements harmonize with it. In general, it may be said that the effect that an alloying element has upon graphitization depends upon the effect that it has upon the relative position of the Atm and Acm lines. Silicon, as has been shown, spreads the lines farther apart thereby assisting graphitization. Nickel, titanium and aluminum are among the elements that probably form unstable carbides. The unstable carbides, like SiC, give an excess of carbon in solution which tends toward precipitation of temper carbon and an acceleration of graphitization. Briner and Senglet[5] said that the reaction,

$$Al_4C_3 \rightleftharpoons 4\ Al + 3\ C,$$

is reversible and that the dissociation begins below 540°C. This fact leads to the conclusion that aluminum spreads the Atm and

Acm lines farther apart. Carbides of gold, copper, and platinum have been discussed in the literature. Even if they do exist, they would not be expected to occur in abundance in cast iron. H. Moisson[31] reports that carbon is dissolved by copper at its boiling point, and rejected as the metal solidifies. A very small amount of copper carbide, if it were unstable, would be sufficient to explain the slight accelerating effect of copper. On the other hand, if the carbide did not exist the effect could be explained on the basis that the metal diluted the iron and consequently reduced the activity of the iron. This reduced activity would cause a shift in equation (1) toward the right to restore equilibrium. If it is true that this acceleration is brought about by dilution, the same atomic per cent of each of the elements which do not form carbides would have the same effect. Elements which retard graphitization usually form very stable carbides. Among these elements may be mentioned molybdenum, tungsten, manganese, vanadium and chromium. These elements may not only owe their effects to the stability of the carbides, but also to the formation of sulfides, phosphides and silicides. It is thought that these elements, by reacting with the impurities in ordinary cast iron, shift the Atm line closer to the Acm line.

In a consideration of the effect of the various gases, it may again be pointed out that anything that will affect any of the equilibria already proposed may either accelerate or retard graphitization. Carbon dioxide speeds up the process because of mass action toward the right in equation (2). Conversely, carbon monoxide aids in shifting the equation toward the left reducing the rate of malleabilization. It is reported that hydrogen almost, if not entirely, stops graphitization. This unusual retardation may be explained in two ways: (1) Hydrogen reduces carbon dioxide to carbon monoxide which opposes the process. (2) It is absorbed on the surface of the carbon as fast as the carbon is precipitated. It is known that certain types of carbon will absorb many volumes of hydrogen. In case this absorption took place the hydrogen concentration would be very great at the surface and, hence, the solution would not be in contact with solid carbon and equilibrium (4) would be annihilated. At least, experimental work shows that hydrogen is soluble to a fairly great extent in iron. Since it is soluble in iron there would be a great chance that it is absorbed on the temper carbon. To show that hydrogen does have intimate contact with the carbon it may be said that, as early as 1867, Graham[15], in his work with meteoric iron, showed that at some time a considerable amount of hydrogen had been absorbed. Cailletet[6], and Troost and Hautefeuille[50] corroborate Graham's work by showing that hydrogen is retained by cast iron and steel when heated in hydrogen to 800°C. As before mentioned, graphitization does not proceed readily until intimate contact is had between the temper carbon and the solid solution. If the above assumption is correct, there could never be any appreciable contact between the two phases when hydrogen is present, and consequently the process would indeed be slow. After heat treating for many hours, it would be possible to have very small carbon spots which might even defy microscopical methods of detecting. It may even be possible for hydrogen to react with this carbon to form methane and some other hydrocarbons. Methane and ammonia have a similar effect to hydrogen on graphitization. Their effects may be explained by the dissociation into carbon and hydrogen, and nitrogen and hydrogen respectively. Nitrogen and oxygen slightly retard graphitization probably on account of either diluting the carbon carrying gases already present or being absorbed on the carbon. If this absorption takes place it is to a much lesser degree than that of hydrogen. Oxygen may also tend to prevent the precipitation of carbon by opposing the decomposition of carbon monoxide into carbon and carbon dioxide. The opposition would come from the oxidation of the monoxide to the dioxide. Air being made up chiefly of oxygen and nitrogen has a similar effect.

Packing mediums owe their effects, with little doubt, to the type of gases produced. Carbonates, such as barium carbonate, on being heated produce an atmosphere of carbon dioxide, which, of course, speeds up the process.

The temperature at which graphitization takes place is perhaps one of the most vital factors to consider. Increased temperature causes a faster dynamic equilibrium in each of the equations (3) and (4). Thus, more excess carbon is produced in the solution in a certain length of time, and therefore it can separate more quickly. The writer agrees that the effect of increasing the tapping temperature is due to the expulsion of the carbon-carrying gases. After their complete expulsion, graphitization must take place according to equation (1), since it would be impossible to have reaction (2). Super-heating the melt and using a constant tapping temperature causes an acceleration in the speed of graphitization[52] with the formation of smaller graphite particles. The high temperature was sufficient to expel greater quantities of the absorbed gases among which were carbon monoxide and hydrogen. On cooling to the tapping temperature the iron could absorb only those gases which were in the atmosphere immediately over the surface of the metal. As a consequence, at least some of the carbon dioxide which was expelled on heating was reabsorbed on cooling but not so with either of the other gases. There were more and smaller graphite particles because of the deficiency in carbon dioxide which according to equations (2) and (6) acts as a carbon carrier. Rates of cooling naturally affect graphitization because of the different amount of surface contact between the cementite and the austenite. For instance, prequenching white cast iron breaks it up into finer grains of fragmental "cementite" and "austenites" which have a great deal more surface exposed to each other. This sample of smaller grains gives a faster dynamic equilibrium between the dissolved Fe_3C and cementite.

Recapitulating, graphitization is affected by the following factors in the manner indicated:

1. Alloying elements either retard or accelerate depending on the type of carbide or carbides formed.

2. Gases, such as hydrogen and others which will yield hydrogen at the graphitizing temperature, retard the process almost to the point of stopping it. Gases, like oxygen and nitrogen, have a slight retarding effect. Carbon dioxide causes an acceleration.
3. The rate of graphitization increases with rise in annealing temperature.
4. The ease of graphitization lessens with higher tapping temperature.
5. Super-heating the melt favors graphitization.
6. The faster the rate of cooling of the casting the faster will graphitization proceed.

IV. EXPERIMENTAL PROCEDURE AND DATA

A. Preparation of Alloys

The materials used in the preparation of the alloys used in this investigation consisted of commercial white cast iron test bars, ferro-manganese, ferro-tungsten and powdered graphite.

Two sets of the commercial cast iron test bars were used which showed the following composition:

Table VIII

Element	Weight Per Cent		
	Set No. 1 Reported by Henderson		Set No. 2 Manufacturer's analysis
Carbon	2.58	2.63	2.46
Silicon	0.78	0.78	0.90
Manganese	0.19	0.21	0.19
Sulfur	0.034	0.032	0.036
Phosphorus	0.154	0.155	0.172

The ferro-manganese contained about 80 per cent manganese.

The ferro-tungsten, as reported by the manufacturers, was of the following composition:

W	73.23%	S	0.54%
Si	0.42%	P	0.015%
C	0.59%	Mn	0.19%

5000 grams of the commercial white cast iron base were melted in a small plumbage crucible by means of a 35 KW Ajax Northrup electric furnace. Twenty five minutes after the run was started, carbon to the extent of one-tenth per cent of the total mass, and calculated amounts of ferro-manganese and ferro-tungsten were added to the molten metal. Immediately after this addition, the melt was stirred with an Armco rod. About ten minutes later, the melt was poured, in some cases, into wet sand molds and, in other cases, into dry sand molds. The dry sand molds had been allowed to dry for twenty four hours in a rather dry room. In each case, the bars which were poured into the wet molds were used for experimental heat treatment; while those of the dry molds were used for physical tests. The molds containing the cast iron were permitted to stand for twenty-four hours before being broken. This period of time, though probably unnecessary, gave ample assurance that the bars of different composition had the same cooling treatment. The pouring temperature, as determined by a Leeds and Northrup optical pyrometer, was in each case slightly above 1300°C.

Four casts consisting of nine bars were made for each composition. The first cast which was made from the test bars of Set No. 1, and poured into wet molds, consisted of three bars; while the other three cast, which were made from the bars of Set No. 2 and poured into dry molds, consisted of two bars per cast. The former castings were broken into convenient lengths of approximately one inch. A specimen about 5 inches long was reserved from each of these castings for chemical analysis. The one-inch pieces were used in the experimental heat treatment. As previously mentioned the latter castings were used for testing the physical properties. The "as cast" bars which were broken showed a white fracture and a shrink or segregation, in many cases, near the center.

B. Chemical Analysis

The chemical analyses were carried out according to the standards of the American Society for Testing Materials. Tungsten was determined by the acid-digestion-cinchonine method in which the tungsten was finally weighed as WO_3. Manganese was determined by the sodium bismuthate method. Sulfur was determined gravimetrically by precipitating it as $BaSO_4$. Silicon was determined by the nitro-sulfuric and dehydration method. Since Henderson, using the same base metal, found that the sulfur content of seven different alloys was very close to constant at 0.035 per cent and since the writer found that four of these alloys, made from the same base metal, also contained .035 per cent sulfur, it was assumed that the other alloys would also contain very close to this same amount. Therefore, the sulfur determinations were made for only four of the twelve alloys. Likewise, it was deemed inadvisable to make the phosphorus determination because other investigators, using the same base metal, found that the phosphorus content remained practically constant at 0.15 per cent. The carbon determination was made by direct combustion in a stream of oxygen, ascarite being used as the absorbent. The analyses follow:

Table IX

Melt No.			Analyses		
	W(%)	Mn(%)	Si(%)	S(%)	C(%)
25	0.91	0.93	0.84	0.035	2.69
	0.92	0.96	0.84	0.037	2.69
26	2.78	0.87	0.84	---	2.64
	2.79	0.88	0.85		2.64
27	4.89	0.90	0.86		2.52
	4.94	0.88	0.83	---	2.53
28	0.87	2.85	0.82		
	0.86	2.89	0.87	---	2.65
29	2.65	2.65	0.88		
	2.58	2.66	0.88	---	2.59
30	4.32	2.87	0.86		
	4.21	2.83	0.83	---	2.59
31	0.92	4.59	---		
	0.95	4.59	0.79	---	2.66
32	2.61	4.48	0.78		
	2.68	4.46	0.79	---	2.65
33		0.96	0.84	0.038	2.61
	0.00	0.94	0.84	0.037	2.56
34		3.29	0.83	0.035	2.80
	---	3.27	0.84	0.036	2.80

35		4.99	0.84	0.035	2.84
	---	5.01	0.81	0.034	2.84
36	4.14	4.28			
	4.21	4.24	---	---	2.61

It is interesting to note a comparison of the analyses of tungsten and manganese with the theoretical amounts of these elements expected. Apparently very little, if any, of the manganese or tungsten goes into the slag during the 35 minutes of melting. The agreement between the theoretical values and the values actually found is remarkable when it is remembered that the weighings of the alloy additions were rather roughly made and too, the process of melting causes some constituents to migrate to the slag. The comparison of these data follows:

Table X

Sample No.	Mn(Found)	Mn (Theoretical)	W (Found)	W.Theoretical
25	0.945	0.96	0.91	0.96
26	0.88	0.94	2.78	2.78
27	0.89	0.92	4.91	4.52
28	2.87	2.83	0.87	0.94
29	2.64	2.76	2.63	2.72
30	2.85	2.71	4.27	4.42
31	4.59	4.63	0.93	0.92
32	4.47	4.53	2.65	2.65
33	0.95	1.00	---	0.00
34	3.28	3.25	---	0.00
35	5.01	4.99	---	0.00
36	4.26	4.42	4.18	4.32

The bars which were used for the physical properties were not analyzed. A careful attempt was made to exactly duplicate the method of melting, pouring, etc., as that used above in the preparation of the bars for experimental heat treatment. The results in Table X indicate that analyzing these bars would be a mere waste of time.

C. Critical Points

A study was made of the effects of manganese and tungsten, in a few of the alloys, upon the critical points. Only five of the alloys could be used due to the fact that the remaining ones were indeed too hard for drilling, and consequently there was no convenient way of getting the differential thermocouple into the sample. As previously mentioned, these data were obtained in order to consider the feasibility of proceeding with the graphitization through the second stage and to determine the temperature at which it should be done. R. S. Archer[1] has compiled the following data on critical points of white cast iron:

Table XI

Temperature ($^\circ$C)		Silicon (%)	Observer
Ar, point	Ac, Point		
740-750		1.14	Wurst and Petersen
730		0.97	Hague and Turner
734		1.19	Hague and Turner
700	815	1.10	Charpy and Cornu-Thernard

The writer, using a Leeds and Northrup apparatus designed for critical point determinations, obtained 729°C. for the Ar_1 point and 797°C. for the Ac_1 point in the white cast iron base which contained 2.60 per cent carbon, 0.78 per cent silicon and 0.20 per cent manganese. These results seem to be in quite close agreement with those obtained by Hague and Turner.

From the data of Table XII, it will be noted that the critical points are lowered with the addition of manganese, while tungsten has little effect. Manganese, of course, does not have such a great effect when increased from 0.20 to 1.00 per cent due to the fact that the manganese has perhaps united with sulfur, phosphorus or silicon. It is to be expected that the critical points of the samples which contain as much as 3 per cent manganese are much lower than 700°C.

Table XII

Melt No.	Mn (%)	W (%)	Si (%)	Ar_1	Ac_1
Cast	0.20	---	0.78	729°C.	797°C.
25	0.945	0.91	0.84	712°C.	792°C.
26	0.88	2.78	0.85	710°C.	794°C.
27	0.89	4.91	0.84	709°C.	794°C.
33	0.95	---	0.84	717°C.	789°C.

D. Heat Treatment

The heat treatment was made in a Hump annealing furnace at 925°C. The temperature was determined by means of iron-constantan thermocouples and was controlled by a Leeds and Northrup Automatic Recorder. A Leeds and Northrup Student Potentiometer was used frequently to check the accuracy of the automatic recorder. In order to be more certain that tho annealing temperature was known, the readings of the iron-constantan thermocouples were checked against a standard platinum-rhodium thermocouple. The iron-constantan thermocouples were replaced each 48 hours due to oxidation of the iron.

As has been said, the purpose of this investigation was to determine the effects of manganese and tungsten on the rates of graphitization through the first stage. However, an attempt was made to carry the graphitization of a few of the samples through the second stage by cooling them slowly (after the first stage had been completed) from 925°C. to 704°C. and, at this point, maintaining constant temperature. The commercial white cast iron, which was used as a reference standard, was completely malleabilized after heating 9 hours at 925°C., cooling to 704°C. in 5 hours and heating 5 hours at the latter temperature. The samples containing manganese and some of those containing both manganese and tungsten, whose A_1 critical point was higher than 704°C., after having been heated a predetermined time at 925°C., were similarly cooled to 704°C. in 5 hours and maintained at this temperature for 40 hours. None of these samples except No. 33

showed any marked progress toward graphitization in the second stage. Consequently, in view of this fact and others which have previously been discussed, further efforts to graphitize these samples through the second stage were abandoned.

The samples, which were about one inch in length, were packed either in iron gas pipes capped on one end or in small plumbago crucibles with gas carbon of about 20 mesh. The gas carbon served in the production of a reducing atmosphere, which would prevent undue oxidation of the samples. The plumbago crucibles were soon found to be entirely unsatisfactory for the longer heat treatments and were used only for those samples requiring less than 20 hours. Due to their porosity oxygen from the air had a rather unlimited circulation around the specimens being heat treated. Those few alloys which were heated for about 100 hours in the plumbago crucibles were converted, in each case, in to merely swollen masses of oxides, which in some cases still contained a small core of the original. On the other hand, the iron pipes were sufficient to preserve the sample even when heated for 200 hours. It was noted, however, even after all of these precautions that considerable decarburization took place near the surface.

Since only the microscopical method was used to determine the end of graphitization, it was thought to be necessary to make preliminary study to ascertain the approximate time for completion of the process for each of the alloys. In order to do this, one sample of each of the alloys was packed in each of two 2 x 8 in. iron gas pipes with gas carbon and then placed in the annealing furnace, which had previously attained the annealing temperature. After the pipes were placed in the furnace its temperature usually fell to about 775°C., finally regaining the former height after the expiration of some 30 minutes. The time at which the furnace was again at 925°C. was recorded as that of the beginning of heat treatment. One pipe, which will be designated as pipe No. 1, was taken from the furnace at the end of 24 hours and permitted to cool in air to room temperature. After the pipe with its contents were cooled, the samples were examined microscopically as will be explained in a latter section of this paper. Those samples which still contained massive cementite were repacked in the same pipe and replaced in the furnace. Pipe No. 2 was removed at the end of 48 hours and its contents similarly inspected. As in the former case, those alloys which showed the presence of massive cementite were repacked and returned to the furnace. This process of removing the pipes alternately every 24 hours continued until each specimen had been rendered completely void of free cementite.

Now having found the approximate time samples were packed in individual pipes (2 x 8 inches) or, if convenient, they were packed in groups in larger pipes and placed in the furnace. After continuing the heat treatment for approximately the same length of time as that found in the preliminary study and cooling as before, it was found that none of the samples contained massive cementite. Shorter heat treatments were made until, in each case, the samples contained free cementite. Successive runs were made until the actual time for completing the process was determined. About eight samples of each composition received this treatment to either determine or confirm the time necessary for the completion of the first stage of graphitization.

Table XIII gives a summary of the heat treatment of the various alloys. The complete data are given for melt No. 30 only.

Table XIII

Melt No.	Sample No.	Hours at 925°C.	Progress of Graphitization
25	3	6	Much cementite
25	1	11	Almost complete
25	2	12	Complete
25	4	15	Complete
26	11	11	Incomplete
26	15	16 1/2	Almost complete
26	14	18	Complete
26	13	22	Complete
27	21	11	Incomplete
27	24	20 1/2	Almost complete
27	26	23	Almost complete
27	25	25	Complete
28	31	90	Almost complete
28	36	93 1/2	Complete
28	32	121 1/2	Complete
29	45	60	Almost complete
29	47	65	Complete
29	46	70	Complete
30	51	48	Incomplete
30	52	48	Incomplete
30	55	50	Incomplete
30	56	51	Almost complete
30	54	54	Complete
30	57	55	Complete
30	53	60	Complete
30	58	76	Complete
31	65	60	Incomplete
31	67	65	Almost complete
31	66	70	Complete
31	64	71	Complete
32	73	60	Incomplete
32	75	65	Complete
32	74	70	Complete
33	81	3	Incomplete
33	84	5	Almost Complete
33	86	6 1/4	Almost complete
33	87	8	Complete
33	88	8	Complete

Table XIII (cont'd)

Melt No.	Sample No.	Hours at 925°C.	Progress of Graphitization
34	92	90	Incomplete
34	96	90	Incomplete
34	95	95	Complete
34	94	100	Complete
35	103	71	Incomplete
35	105	75	Incomplete
35	104	80	Complete
35	102	90	Complete
36	114	42	Incomplete
36	113	44	Almost complete
36	115	44	Complete
36	116	46	Almost complete
36	111	48	Complete
36	117	48	Complete
cast	b	3	Incomplete
cast	c	5 1/2	Almost complete
cast	b	8	Complete
cast	a	11	Complete

It is interesting to note the anomolous results which were obtained in the preliminary study. In Table XIV these values are contrasted with those finally determined. The final value is taken as a rough average of those values which are near the end-point. It should be pointed out again that in the preliminary treatment the samples were only checked each 24 hours. Consequently, the preliminary value for those samples which required less than 24 hours are omitted.

Table XIV

Summary

Melt No.	W(%)	Mn(%)	Time in Hours Preliminary	Time in Hours Final
25	0.91	0.94	----	12
26	2.78	0.87	----	17
27	4.91	0.89	----	24
28	0.86	2.87	192	93
29	2.61	2.63	144	65
30	4.26	2.85	120	53
31	0.92	4.59	144	68
32	2.64	4.47	144	62
33	----	0.95	----	8
34	----	3.28	192	93
35	----	5.00	168	78
36	4.17	4.26	72	46
cast	----	0.20	----	8

Samples from melts 25, 26, 27, 33 and cast were not returned to the furnace for further heat treatment in the preliminary study, and therefore, offer no means for comparison or contrast.

E. Photomicrographs

To determine the end-point of graphitization the samples were polished on a rough emery wheel to a depth of about 1/8 inch in order to insure the elimination of surface heterogeneity. After continuing the polishing with less severe abrading agents until the sample was well free of scratches, the specimen was etched with sodium picrates which showed the presence or absence of massive cementite. This etch was removed on the polishing wheels and then a nitric acid-ethyl alcohol (5 per cent nitric acid by volume) etch was administered in order to determine the nature of the matrix which was in most cases martensitic. Extreme difficulty was experienced in successfully obtaining and retaining the latter etch with a clear, well defined structure. Many of the samples were over-etched in one second. This rapid etching is probably due to the presence of the manganese. The fact that these samples corroded very rapidly required undue solicitude in attempting to obtain good photomicrographs.

Photomicrographs of some of the alloys are presented that may corroborate the data already given and show the structure of the alloys as cast, during the progress, and completion of graphitization. The photomicrographs of white cast iron are presented as a basis of comparison. In each case the photomicrograph was taken from a portion of the sample which showed the maximum amount of cementite, except, of course, in the unetched samples in which none was discernible.

The alloys as cast, unlike ordinary white cast iron, did not contain pearlite. All of those which were poured in dry sand molds consisted of cementite and martensite (Fig. 16). However, the more rapid cooling produced by the green molds was sufficient to partially retain austenite in melts 30, 32 and 36. In fact, alloys 32 and 36 contained so much austenite that they hardly exerted any force on a magnet. Alloy 30 had considerably less austenite; it was chiefly martensite. These structures are shown in Fig. 14, 17 and 18. There was a great tendency for dendritic segregation in all of the alloys. This phenomenon is exemplified by Fig. 15. The photomicrograph was taken from a portion of alloy 31 which showed the maximum degree of segregation. Portions could be found in all of the remaining alloys which also showed the presence of dendrites. The photomicrographs of the as cast samples of the remaining alloys, which are shown, were taken from regions in which dendrites were not outstanding.

Fig. 4 illustrates the presence of the characteristic "bull's eye" structure. This structure consists of temper carbon spots around which free ferrite has deposited. According to Hayes' theory of graphitization, this ring of ferrite is deposited when the sample containing the solid solution at the stable eutectoid point is cooled rapidly enough to prevent the simultaneous precipitation of the entire solid solution as ferrite and temper carbon. Ferrite is deposited as the specimen is cooled from the stable to the metastable eutectoid point. This is represented in Fig. 1 by the line SC. No "bull's eye" structure was evident in any of the alloys. This fact tends to prove that the line SC, because of the addition of manganese or tungsten or both has become indeed short and insufficient ferrite is deposited to be detected, or that S coincides with C. At any rate, the sum of the effects of the additional elements is to cause the carbon-from-carbon-solubility line to lie more closely to the carbon-from-iron carbide solubility line.

All of the annealed alloys contained a martensitic matrix. Fig. 19 is selected to show the typical structure. Of course graphitization, as has beenobserved by many investigators, proceeds from the center out to the surface of the sample. Fig. 20

shows a portion of alloy 32 near the surface and also illustrates the sodium picrate etch. The center of the sample was completely graphitized through the first stage, and consequently no cementite was detected, but, as clearly shown by the photomicrograph, the region near the surface contained much cementite and is far from completion.

Fig. 5, 9, 21, 22 and 23 serve to indicate the size of carbon spots that was obtained in the various alloys. Either one or both of two factors may be responsible for the fact that the spots in some samples are considerably larger than those in another. First, the prolonged heating may serve to reduce the size by loss of carbon in the form of CO or CO_2. Second, the alloy addition may serve to refine the structure which would favor more nuclei of deposition and smaller carbon spots. The carbon spots in Figs. 5, 9, and 23 are quite large and are about the same size in each sample, while those of Fig. 21 and 23, though about the same size in the two samples, are much smaller than those in the former mentioned alloys. In general, it may be said that the longer the required heat treatment the smaller and more numerous are the carbon spots.

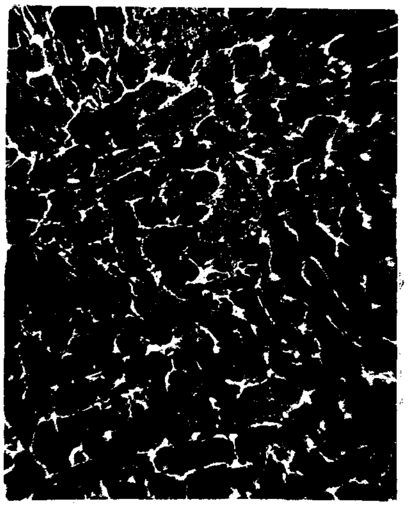

Fig. 2 100 X
White Cast
As Cast

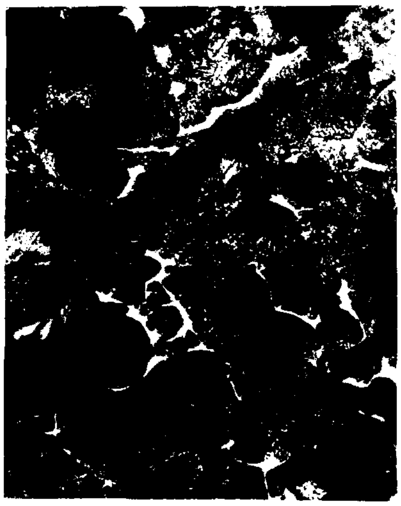

Fig. 3 100 X
3 hours at 925°C.
White Cast

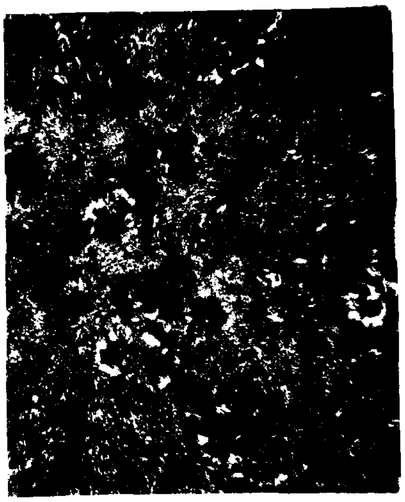

Fig. 4 100 X
8 hours at 925°C.
White Cast

Fig. 5 100 X
8 hours at 925° C.
Unetched
White Cast

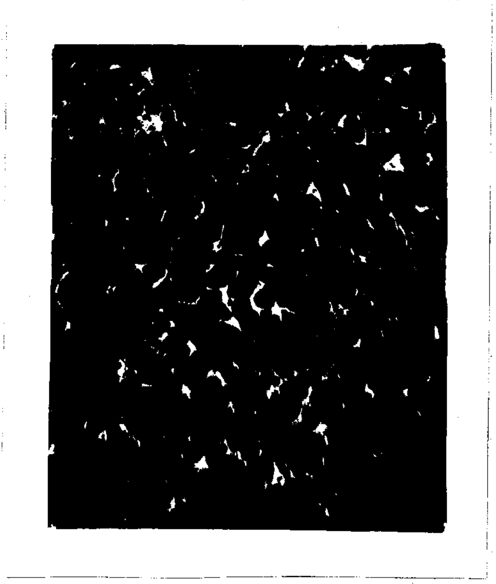

Fig. 6 100 X
Melt No. 25
6 hours at 925°C.

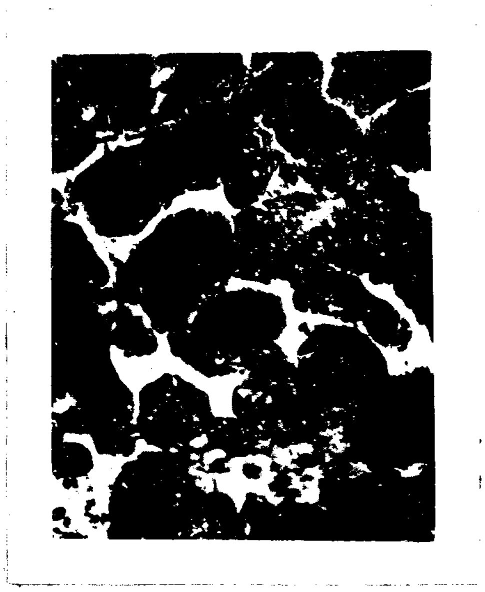

Fig. 7 500 X
Melt No. 25
6 hours at 925°C.

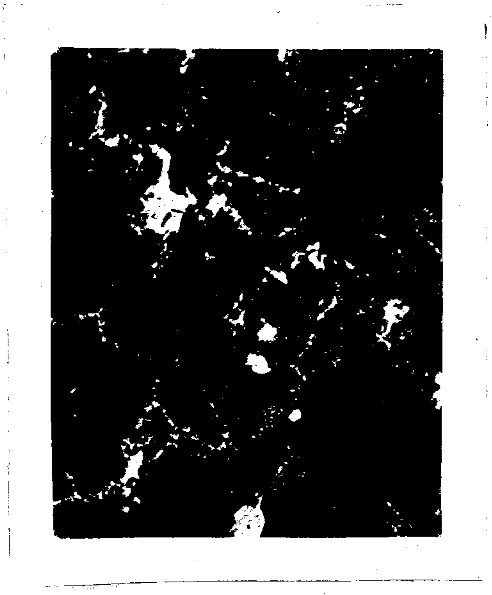

Fig. 8 250 X
Melt No. 25
11 hours at 925°C.

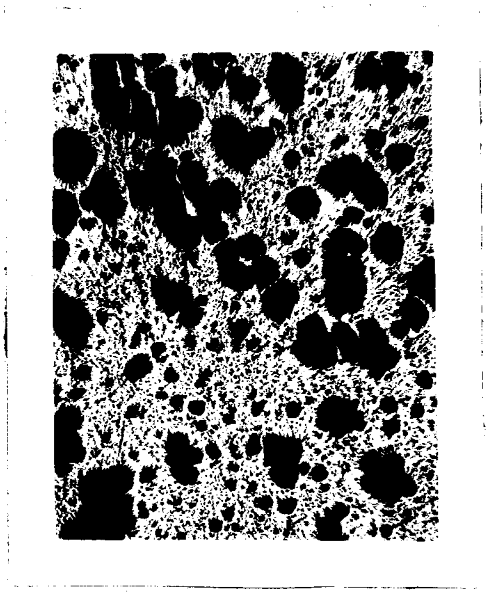

Fig. 9 100 X
Melt No. 25
12 hours at 925°C.
Unetched

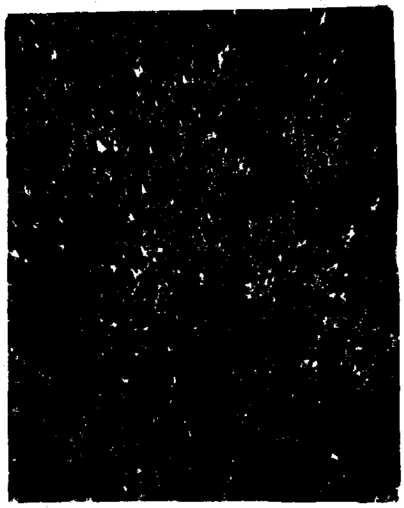

Fig. 10 100 X
Melt No. 25
12 hours at 925°C.

Fig. 11 750 X
Melt No. 27
As Cast

Fig. 12 100 X
Melt No. 28
As Cast

Fig. 13 100 X
Melt No. 29
As Cast

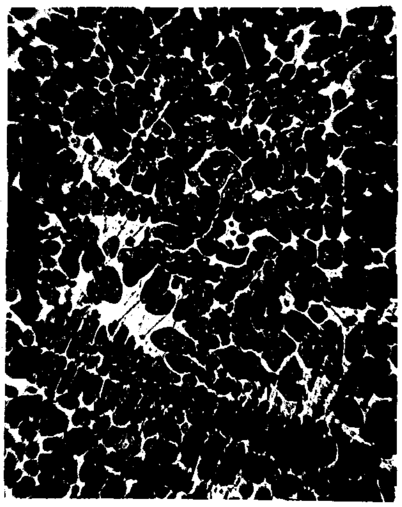

Fig. 14 100 X
Melt No. 30
As Cast

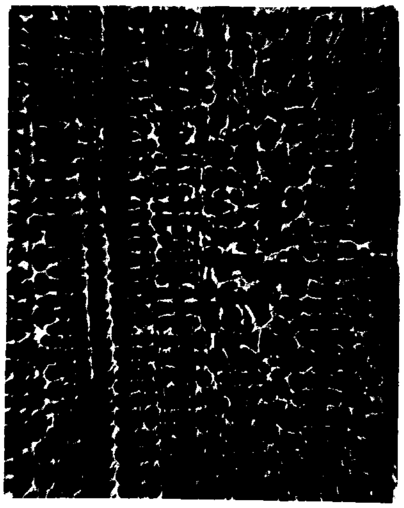

Fig. 15 100 X
Melt No. 31
As Cast

Fig. 16 250 X
Melt No. 31
As Cast

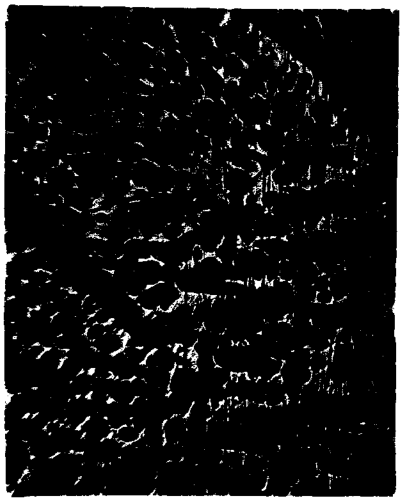

Fig. 17 100 X
Melt No. 32
As Cast

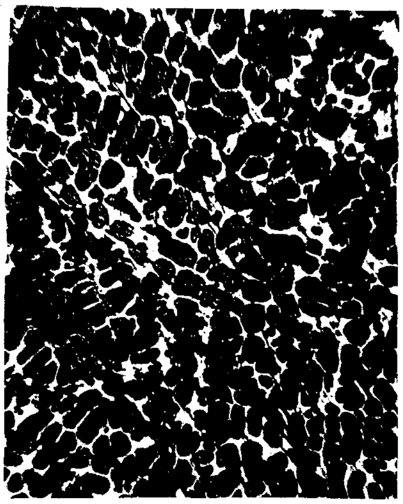

Fig. 18 100 X
Melt No. 36
As Cast

Fig. 19 100 X
Melt No. 28
93.5 hours at 925°C.

Fig. 20 500 X
Melt No. 32
60 hours at 925°C.
Sodium picrate etch

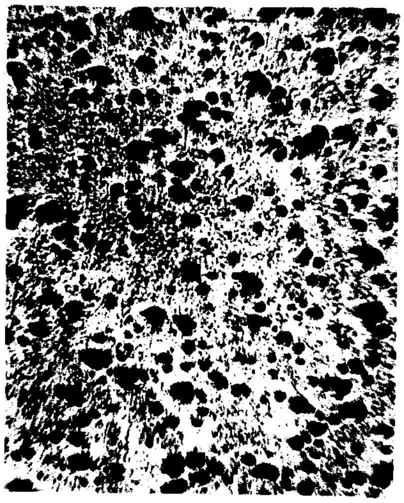

Fig. 21 100 X
Melt No. 32
71 hours at 925°C.
Unetched

Fig. 22 100 X
Melt No. 28
93.5 hours at 925°C.
Unetched

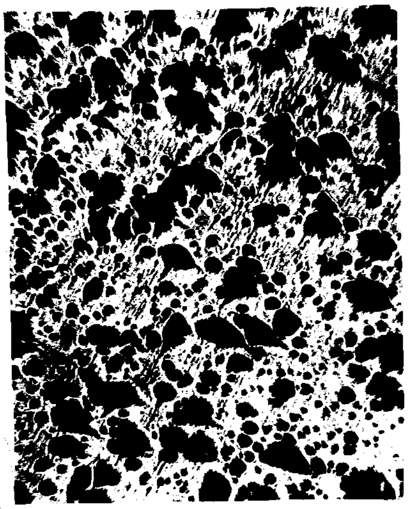

Fig. 23 100 X
Melt No. 33
8 hours at 925°C.

F. Physical Properties

These tests were performed with 14 x 5/8 inch bars. As previously mentioned, six bars of each composition were cast for physical property tests two being cast from each melt. A summary of these data appears in Table XV. In this table the arabic part of the melt number signifies the composition while the letter which immediately follows indicates a particular melt. To make this clear let us take some melt number as 27 X. The "27" indicates that this alloy has approximately the same composition as melt No. 27 which was used in the experimental heat treatment. The "X" signifies a different but duplicate cast. In some cases there will be found the letter H or Q following this first letter. H means that the bar was heat treated at 925°C. for 1 1/2 times as long as the experimental values found for the bars which were cast in green sand molds. The bars were heated this extra time to be certain that they were completely graphitized through the first stage. Q means that the bar, after the above heat treatment, was reheated to 775°C., held at this temperature for thirty minutes, and then quenched in water which was 24°C.

The bars were cleaned of all sand and grit by polishing with a wire-brush wheel and then by removing, perhaps, 1/32 inch of the outer skin with a rough emery wheel. After the bars had been cleaned, they were packed with gas carbon in 3 x 14 inch iron pipes. Four bars of the same composition were usually packed in the same pipe.

A hand operated machine was used for making the tensile strength tests; the same machine was used for measuring the Brinell hardness. Some of the bars, after quenching, were so brittle that it was found impossible to obtain their Brinell hardness on account of the ease with which the samples were fractured. No appreciable ductility was evident; therefore no data are included on elongation. The elastic limit was the same as the tensile strength.

Some of the bars were found to contain blow holes. No tests were made with these bars nor were other bars poured to take their place. It is believed that the quenched bars contained many very small cracks which accounts for the discrepancy in some of the data.

Table XV

Sample No.	Brinell Hardness	Mean Diameter inches	Tensile Strength: lbs./in^2
C - Y	418	0.536	30,400
C - Z	375	0.546	35,500
C-XH	217	0.640	52,250
CZH	217	0.625	49,000
CXQ	no test		
CY_2	no test		
25YH	305	0.632	62,000
25WH	---	0.620	54,000
25ZQ	345	0.620	11,000
25WQ	351	0.645	13,700
26YH	345	0.642	70,000
26XH	340	0.620	66,500
26YQ	418	0.642	17,900
26ZQ	418	0.635	17,200
27Z	444	0.500	33,700
27Y	435	0.525	38,400
27XH	375	0.633	64,200
27ZH	362	0.580	56,700
27XQ	321	---	---
27YQ	330	0.630	42,000
28YH	330	0.643	42,900
28ZH	336	0.642	46,000
28XQ		0.630	42,700
28YQ		0.645	50,100
29Y	600	0.538	26,600
29Z	600	0.545	28,000
29XH	345	0.619	47,600
29ZH	340	0.609	41,700
29XQ	508	0.648	31,800
29YQ	512	0.620	26,500

Table XV (cont'd.)

Sample No.	Brinell Hardness	Mean Diameter inches	Tensile Strength lbs./in²
30A	512	0.612	38,100
30A	506	0.605	38,000
30XH	332	0.640	44,500
30YH	332	0.650	41,500
30XQ	375	0.642	22,400
30YQ	351	0.656	23,400
31A	560	0.600	28,300
31A	555	0.650	28,100
31XH	351	0.615	39,500
31XH	370	0.600	29,800
31XQ	418	0.625	23,500
32A	540	0.628	22,900
32A	555	0.645	22,700
32YH	460	0.632	27,400
32XH	452	0.645	30,600
32YQ	---	0.618	16,700
33X	418	0.550	35,000
33Z	402		
33YH	277	0.656	57,000
33ZH	272	0.665	56,000
34Z	470	0.568	30,200
34YH	380	0.650	35,000
34XH	387	0.645	31,300
34XQ	---	0.652	12,750
35Y	520	0.497	25,700
35Z	505	0.506	24,000
35YH	300	0.655	35,700
35ZQ	---	0.640	13,000
36XH	470	0.600	34,000
36YH	460	0.665	34,800
36XQ	600	0.640	10,800
36YQ	578	0.640	10,800

From the above table, it may be noted that addition of manganese to white cast iron causes an increase in hardness but a decrease in the tensile strength. This is not only true with cast irons containing manganese as the only alloying element, but also true for alloys containing manganese with a constant amount of tungsten. Addition of tungsten causes a slight increase in hardness and also a slight increase in tensile strength. Tungsten has a more pronounced effect in the heat treated alloys. The tensile strength is increased from 56,500 to 68000 lbs./in.^{2} by an addition of 2.78 per cent tungsten when the manganese content is held constant at about one per cent. On the other hand, when the manganese content is raised to about 2.75 per cent, tungsten additions have but slight, if any, effect on either hardness or tensile strength. In the quenched samples containing about one per cent manganese, the tensile strength rises very rapidly with an increase of tungsten. However, it has just the opposite effect when the manganese content is as high as 2.75 per cent.

V. DISCUSSION OF RESULTS

Both manganese and tungsten have been found to favor the formation of carbides in white cast iron. Because of the presence of these carbides more time is required to graphitize samples containing either tungsten, manganese or both than for ordinary commercial white cast iron.

In plotting the time for completion of the first stage of graphitization against the combined percentages of manganese and tungsten curves as shown in Fig. 24 are obtained. The point for zero per cent of the alloying constituents is taken from the work of Hoelscher. Evidantly this point may be much higher indeed as this investigator obtained no graphitization, on heating a sample containing very nearly zero per cent manganese and zero per cent tungsten for 71 hours. Even though a point on the ordinate has not definitely been determined, the 71 hour-point is accepted because, as far as this discussion is concerned, it does not matter whether this point be at 100 hours or at an infinite number of hours. The point which is enclosed in a green circle is taken from Kikuta's work; the points in the red circles are for samples containing zero per cent tungsten. The entire curve from A to C represents the effect of manganese in cast iron. In fact, the whole curve may be considered for manganese alloy cast iron containing no tungsten. Alloys containing about one per cent manganese with a variable amount of tungsten furnish points which fall on EF; those containing above about 2.5 per cent manganese with a variable amount of tungsten give points which fall on CD.

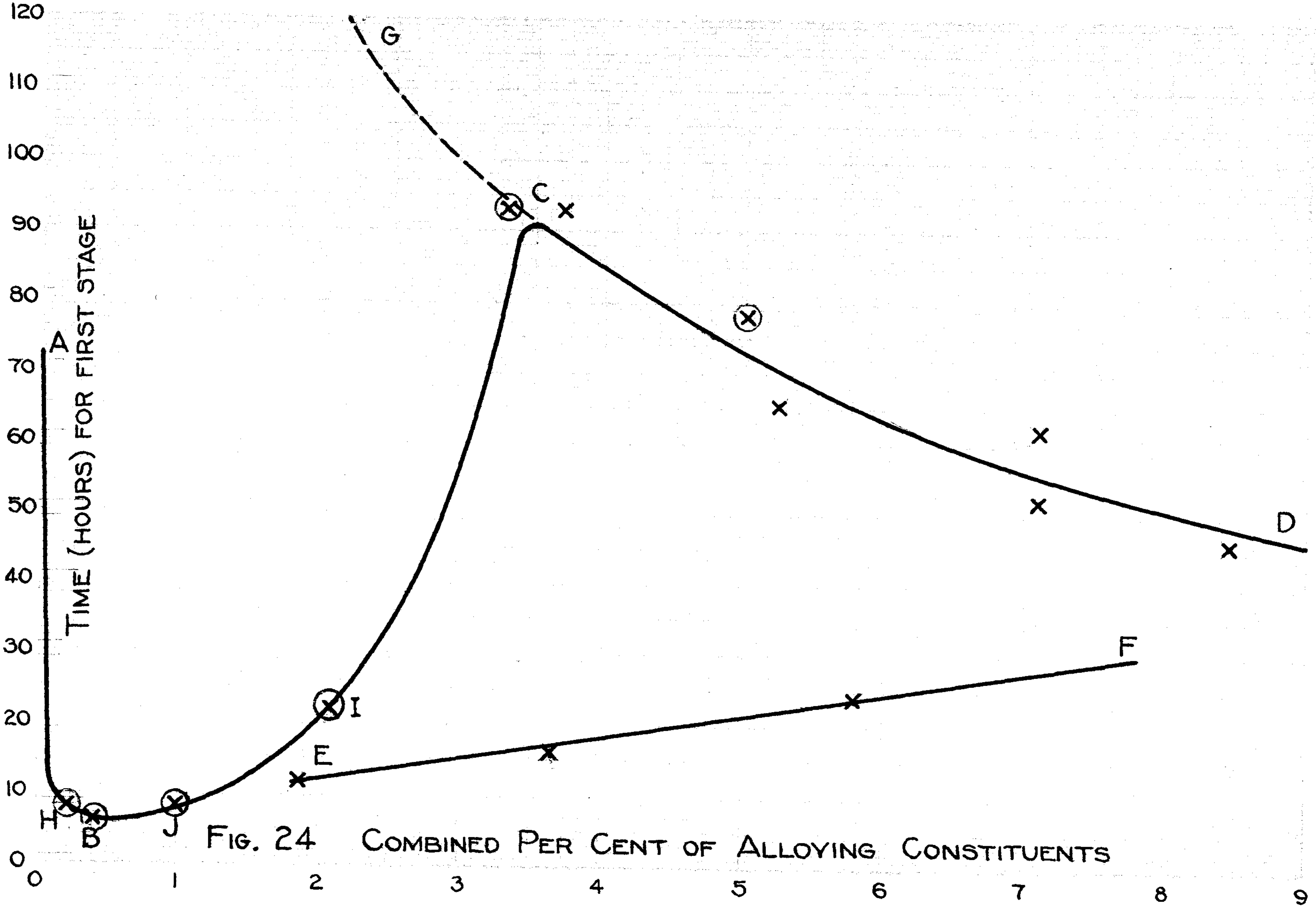

Fig. 24 Combined Per Cent of Alloying Constituents

The point at zero per cent of the alloying element is very high because of the presence of sulfur in the form of FeS. Reference has already been made to the low melting point of this compound. Since it does melt at a lower temperature than the other constituents of cast iron, it will be the last substance to solidify; therefore it appears in the grain boundaries. In the grain boundaries it serves as a film to prevent contact between the austenite and the cementite. As a result, the equilibrium,

$$Fe_3C \text{ (cementite)} \rightleftharpoons Fe_3C \text{ (dissolved)},$$

is impaired to such an extent that graphitization can take place only with great difficulty, if at all.

On increasing the manganese content from zero to 0.2 per cent the curve drops very rapidly from A to H. This part of the curve is due to the destruction of FeS from which MnS is formed. The manganese in forming the small sulfide globules, to which reference has been made, succeeds in destroying the film effect produced by FeS and permits graphitization to proceed. From 0.2 to 1.0 per cent manganese has but little effect on graphitization. As a matter of fact, the sample containing 0.2 per cent required exactly the same amount of time as the one containing 1.0 per cent. It is probable that this part of the curve is due to the formation of some such compound as Mn_3P. There is no apparent reason why, if such a compound is formed, it should not behave similarly to Fe_3P. The formation of Mn_3P is assumed because it is definitely known that manganese will displace iron in FeS which would be indicative of the greater positivity of manganese. From B to C the curve makes a very steep rise which, of course, means that the effect of silicon is being compensated by the additional manganese. This retardation could be accomplished by isolation of the silicon in the form of MnSi or by the formation of a more stable carbide which would tend to reduce the amount of the unstable silico carbide present. The curve slopes gradually from C though D. There are two ways of explaining this decrease in the time required: (1) The increasing manganese content serves to widen the austenite area of the Fe-C equilibrium diagram leaving less of the total carbides to decompose. (2) After the manganese has reacted with all of the impurities the system may be thought of as behaving more like the pure Fe-Mn-C systems. If this is the case, CD represents a portion of the true Mn_3C line, and it appears that in these pure alloys that manganese actually accelerates graphitization.

In support of the contention that manganese reacts with impurities other than sulfur, W.P. Fishel[11] finds that on treating a steel sample containing 0.6 per cent carbon and 0.7 per cent manganese with 3 per cent perchloric acid and analyzing the residue for manganese only 1.25 per cent remain. (Note: 0.7 per cent manganese is on the basis of the whole sample; 1.25 per cent is on the basis of the residue). Since the residue is a comparatively small part of the whole, there is relatively little manganese in the residue. The above fact does not necessarily mean that the manganese is in the form of some compound such as those proposed, but may mean that a certain amount of Mn_3C in a state of subdivision was soluble in the acid. It does, however, point to the existence of manganese in the form of compounds other than the carbide and sulfide. A comparison of the tensile strength and hardness tests of the samples containing 1.0 per cent manganese with those containing 0.2 per cent indicates that the element is not entirely in the form of Mn_3C.

In view of the assumption that these compounds form and that CD represents a portion of the Mn_3C line, it follows that the loop ABC is caused by the presence of the impurities, sulfur, phosphorus, and silicon. It has occurred to the writer that, if the amount of these impurities were decreased, this loop should be less pronounced, the minimum occurring considerably above and to the left of B. The maximum would occur at some point between C and G on DC extended. It will be noted that DC has been extended to approach the ordinate asymtotically.

When tungsten is added to manganese alloy cast iron containing between 0.2 and 2.5 per cent manganese, the effect will be such that it will produce a straight line such as EF. FE extended would strike the curve at some point near J, and this point would represent the effect of a manganese alloy with zero per cent tungsten. An extension in the other direction would permit EF to come in contact with CD extended. After contact the two lines would probably coincide. Again it must be made clear that EF is obtained by using alloys containing one per cent manganese with the percentage of tungsten varying from zero upward to about 4.5 per cent. The line CD shows that, regardless of the individual percentages of tungsten and manganese, the combined percentages of these elements is the factor which determines the time for graphitization. In other words, a sample containing 3 per cent manganese and 4 per cent tungsten will require the same length of time as a sample which either contains 5 per cent manganese and 2 per cent tungsten or 7 per cent of the former and zero per cent of the latter. Apparently when the manganese content is high enough to be at or to the right of C, any additional tungsten acts like more manganese. If alloys were used containing 1.5 per cent manganese with varying amounts of tungsten, it is believed that a line above and parallel to EF would be obtained. It is further predicted that an extension of this line, as well as that of EF, would coincide with CD after coming in contact with it. Any other series of alloys containing a constant amount of manganese would give a similar line the location of which would depend on the percentage of manganese.

It may be noted that on increasing the tungsten content from 0.91 to 4.91 per cent in the one per cent manganese alloys the time for graphitization doubles. This is probably a greater effect than the same amount of tungsten would have in an alloy containing approximately 0.2 per cent manganese. This assumption is made because of the belief that tungsten, on account of mass action, reacts with some of the compounds containing manganese and, thereby, allows more manganese to exist in the form of the carbide. There is but little doubt that tungsten will react with the impurities ordinarily found in cast iron. In fact, Moissan[32] describes a compound that is formed when silicon and tungsten are heated together in an electric furnace. He states that the compound is crystalline with a metallic appearance and that it is hard enough to scratch ruby. This compound may account for some of the hardness caused by an addition of tungsten to cast iron. If tungsten reacts with silicon, it is logical to expect it to react also with sulfur and phosphorus since they are each more negative than silicon. A combination of tungsten with these elements would necessarily mean that more manganese could exist in the form of the carbide which would tend to delay the graphitization more than would tungsten cast irons with lower manganese content.

Work is soon to be in progress in this laboratory to determine whether these various series of alloys will behave in conformity with the theory that has been proposed.

VI. SUMMARY

1. The quantitative effect of manganese upon the rate of graphitization of white cast iron at constant temperature has been determined. The manganese content varied from 0.2 to 5 per cent.

2. The quantitative effect of a combination of tungsten and manganese in alloy cast iron, in which the tungsten varied from 0.87 to 4.91 per cent and the manganese varied from 0.88 to 4.59 per cent has also been determined.

3. Manganese, when added to commercial white cast iron, has little effect until its content exceeds one per cent. From one to about three per cent it retards graphitization very strongly. As the amount is increased above 3 per cent, the time for complete graphitization is gradually reduced.

4. Tungsten in combination with one per cent manganese retards graphitization slightly. When in combination with as much as 2.5 per cent manganese, it serves to accelerate the process.

5. When the manganese content is 2.5 per cent, the same effect may be produced by addition of either more manganese or the same per cent of tungsten, which shows that tungsten acts like manganese in these alloys.

6. White cast iron may be graphitized much more quickly by continuous heating than it can by interrupted heating. Specimens which required ordinarily 93 hours of continuous

heating at 925°C. required 192 hours of heating in periods of 24 hours at the same temperature. At the end of each 24 hour period the samples were allowed to cool rather slowly to room temperature.

7. In attempting to prepare samples for critical point determinations, it was found that any of the alloys which contained as much as 2.5 per cent manganese were too hard to drill even after being completely graphitized through the first stage.

8. Manganese lowers the critical points; while tungsten has little effect.

9. The cast iron bars which contained as much as 2.5 per cent manganese were exceptionally brittle. In fact, they were so brittle that much difficulty was had in obtaining the Brinell hardness due to the ease with which they fractured.

10. Both tungsten and manganese increased the hardness in white cast iron. Manganese causes a decrease in tenstile strength both in the samples containing manganese as the only alloying element and also in those containing tungsten. Tungsten causes a slight increase in tensile strength.

11. In the heat treated alloys tungsten increases the tensile strength to a much more marked degree than in the alloys as cast.

12. A general review of the literature concerning the factors which affect graphitization has been made in order to discuss theory in conformity with the facts obtained by other

investigators. Some interpretations of the results of other investigators have been given.

13. Photomicrographs of some of the typical samples have been included to show the various types of structures which were obtained by the different treatments.

14. A curve obtained by plotting the time for complete graphitization against percentage manganese indicates that Fe_3C in pure Fe-C alloys is stable.

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