THE PARALLEL OXIDATION OF CARBON AND CHROMIUM IN LIQUID IRON (1600°C)

by

LYALL FRANKLIN BARNHARDT

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Signature of Author
Department of Metallurgy

Signature of Professor
in Charge of Research

Signature of Chairman of
Departmental Committee on
Graduate Students

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ABSTRACT

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Submitted to the Department of Metallurgy in April, 1965, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

The path followed by carbon and chromium concentrations in liquid iron during oxidation was investigated experimentally by blowing gaseous oxygen on to slag-free iron - chromium - carbon melts at 1600°C in an induction furnace. The carbon oxidation reaction occurred at the surface of the melt, with an initial constant rate of decarburization which was dependent on the rate of oxygen input. The mechanism of this reaction is expressed in the chemical equation:

$$\underline{C} + 1/2\ O_2\ (g) = CO\ (g).$$

During the initial stage, which was characterized by a constant rate of decarburization, carbon oxidized preferentially with no loss of chromium. Beyond this stage, the rate of carbon loss declined rapidly and the oxidation of iron and chromium occurred.

The entry of argon into the furnace atmosphere, during the oxygen blow, lowered the partial pressure of carbon monoxide at the metal surface. This allowed the carbon concentration of the melt to drop far below the equilibrium carbon content for one atmosphere pressure of carbon monoxide. The metal oxide that formed at the gas-metal interface during the oxygen blow contained FeO as well as chromium oxide. The amount of FeO formed was in excess of that dissolved in the equilibrium oxide (Cr_3O_4). Holding, following the oxygen blow, resulted in the continued oxidation of both carbon and chromium, due to the reaction of these elements with excess FeO. The rate of decarburization, beyond the end of the constant rate of carbon loss, is probably controlled by the diffusion of carbon from the bulk metal through a diffusion boundary layer to the melt surface where reaction occurred.

A mechanism for chromium oxidation was suggested that involved the initial formation of FeO, followed by the precipitation of chromium spinel ($FeO{\cdot}Cr_2O_3$) from the FeO as the solubility limit was exceeded. The oxidation of chromium dissolved in liquid nickel was shown to occur with much more difficulty than the oxidation of chromium dissolved in liquid iron.

The experimental oxidation of iron-chromium-carbon melts by air bubbling provided an extended period of declining decarburization rate. This stage of oxidation, characterized by a decreasing rate of carbon loss, was analysed quantitatively, to provide a means to predict the path followed by carbon during oxidation. The effective oxidation of carbon to very low concentration, by means of air bubbling, with relatively small parallel loss of chromium, merits consideration in the commercial decarburization of iron-chromium-carbon melts in stainless steelmaking.

Dr. T. B. King,

Professor of Metallurgy; Head of the Department.

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I. INTRODUCTION

In the melting of stainless steels, a serious problem facing the producer is to secure the oxidation of carbon to very low concentrations (0.01 to 0.05 percent), with maximum retention of chromium in the melt. The use of iron ore for purposes of carbon oxidation, which was common to carbon and low alloy steel practice, proved inadequate in securing these low carbon levels, with chromium in solution in the metal.

In the early nineteen hundred and forties, the use of gaseous oxygen was introduced into stainless steel melting practices. Oxygen blowing had the effect of raising the metal bath temperature to high levels, which provided preferential oxidation of carbon with greater retention of chromium.

The carbon-chromium relationships in liquid iron, in equilibrium with the stable oxide of chromium and one atmosphere pressure of carbon monoxide, have been established through the work of many investigators. This work is discussed in the subsequent chapter. The relationships are published in the literature, showing the limits of decarburization of iron-chromium alloys at atmospheric pressure.

From the carbon-chromium relationships, may be obtained the equilibrium concentration of chromium retained for a particular carbon content and temperature. However, based on the observation by the author of actual furnace practice in the melting of stainless steels, the amount of oxygen used was less than that theoretically required for the formation of carbon monoxide and chromium oxide, in oxidizing from the initial to the final carbon concentration. This was the case for an assumed metal temperature of 1800° and 1850°C. A ceiling temperature for the metal, during the oxygen blow, of approximately 1800°C has been suggested by Hilty, Rassbach, and Crafts,[1] based on a balance attained between the heats of reaction and the furnace radiation losses.

This disagreement between the theoretical and actual oxygen requirements could be caused by several factors, such as:

1. The suggested metal temperature may be too low.
2. The effect of air drawn in by the oxygen stream in augmenting the total supply of oxygen.
3. The limits of decarburization indicated by the established equilibria may not accurately describe the conditions existing in the oxidizing period.

The present work was initiated to examine the change in carbon and chromium concentrations during oxidation by the blowing of gaseous oxygen on to the surface of slag-free iron-chromium-carbon melts, held at a temperature of 1600°C. In the examination of the approach to equilibrium in this manner, it was expected that some light would be shed on the reasons for the above disagreement.

II. RELATED WORK

The reaction between carbon and oxygen in liquid iron is of fundamental importance in steelmaking and has received attention from numerous investigators. The work in this area has been reviewed by Ward[2] and Bodsworth.[3]

A study of the gas-liquid metal reaction with slag-free melts was conducted by Fujii.[4,5,6] Using oxygen -argon mixtures over iron melts containing carbon, he studied the rate of carbon oxidation. Fujii reports that the reaction between carbon and oxygen occurred at the melt surface and the rate was controlled by gaseous diffusion above approximately 0.15 percent carbon. Below this carbon concentration, the rate of carbon oxidation decreased, which was attributed to the shift of rate control to carbon diffusion in the metal.

Baker, Warner, and Jenkins,[7] using the levitation technique, studied the kinetics of decarburization of liquid iron in an oxidizing atmosphere. Starting with initial carbon contents of approximately 5 percent, they demonstrated a constant rate of carbon loss for various carbon dioxide-helium gas mixtures. The rate of carbon loss was shown to be dependent on the gaseous diffusion of carbon dioxide in the mixtures. The rate of carbon removal was extremely high for the situation where gas is flowing past small metal spheres. The reaction site was reported to be the surface of the spherical melt, with no evidence of carbon monoxide bubble nucleation beneath the melt surface.

The investigations of Chen and Chipman[8] provided data concerning the effect of chromium on the activity coefficient of oxygen in liquid iron. Standard free energies were established for the equilibria:

$$FeO.Cr_2O_3\ (s) = Fe(l) + 2\underline{Cr} + 4\underline{O}\ (\text{percent Cr} < 5.5)$$

$$Cr_2O_3\ (s) = 2\underline{Cr} + 3\underline{O}\ (\text{percent Cr} > 5.5)$$

The carbon-chromium relationships in liquid iron were studied by Hilty.[9] In these investigations, oxygen was blown on to the surface of iron-chromium-carbon melts, and the carbon and chromium contents and temperature of the melt were measured. It was demonstrated that at fixed temperature,

$$\left(\frac{\text{percent Cr}}{\text{percent C}}\right)_T = \text{constant}$$

Richardson and Dennis [10] investigated the effect of chromium on the activity coefficient of carbon in liquid iron. A pronounced lowering of the activity coefficient was noted. Agreement with this work was reported by Fuwa and Chipman.[11]

The investigations of Hilty, Forgeng, and Folkman[12] concerned the oxide phases that are in equilibrium with varying levels of chromium concentration in liquid iron. The oxides were established as chromite ($FeO.Cr_2O_3$) up to 2 percent chromium, distorted spinel ($Fe_xCr_{3-x}O_4$) from 2 to 9 percent chromium, and Cr_3O_4 for chromium concentration above 9 percent.

Following the work of Hilty, Forgeng, and Folkman, the data from Chen and Chipman's investigations were reevaluated.[13] By combining with the carbon-oxygen reaction, the standard free energies were available for the equilibria:

$$FeCr_2O_4\ (s) + 4\underline{C} = Fe(l) + 2\underline{Cr} + 4CO\ (g)$$

$$\log K = \frac{-43,270}{T} + 28.21\ (\text{percent Cr} < 9.0)$$

$$Cr_3O_4\ (s) + 4\underline{C} = 3\underline{Cr} + 4CO\ (g)$$

$$\log K = \frac{-46{,}060}{T} + 30.52\ (\text{percent Cr} > 9.0)$$

With the known interaction coefficients with regard to the effect of chromium on the activity of carbon in liquid iron, the carbon percentages for varying levels of chromium concentration, in equilibrium with the stable oxide of chromium, were established, with the assumption that the effective pressure of carbon monoxide is one atmosphere. The results are presented as the limits of decarburization of iron-chromium alloys at atmospheric pressure.[13] When compared with Hilty's[9] data, good agreement was obtained, which supported the assumption of one atmosphere pressure for carbon monoxide.

A summary of the work conducted with regard to the oxidation and reduction periods of the stainless steelmaking process was presented by Hilty, Rassbach, and Crafts.[1] The effect of oxygen input rate on the removal of carbon in this process was considered by Healy and Hilty.[14]

In Figure 1, the carbon-chromium relationships are illustrated for metal temperatures of 1600°, 1700°, and 1800°C, for one atmosphere pressure of carbon monoxide. The path followed by carbon and chromium concentrations in the melt during oxidation, has not been clearly defined. A possible means of approach to the equilibrium composition is indicated by the broken line in Figure 1, starting with an initial concentration of carbon and chromium that is well away from equilibrium. In following this tentative path, carbon oxidation occurs preferentially during the initial stage, followed by an asymptotic approach to the equilibrium line for the temperature involved.

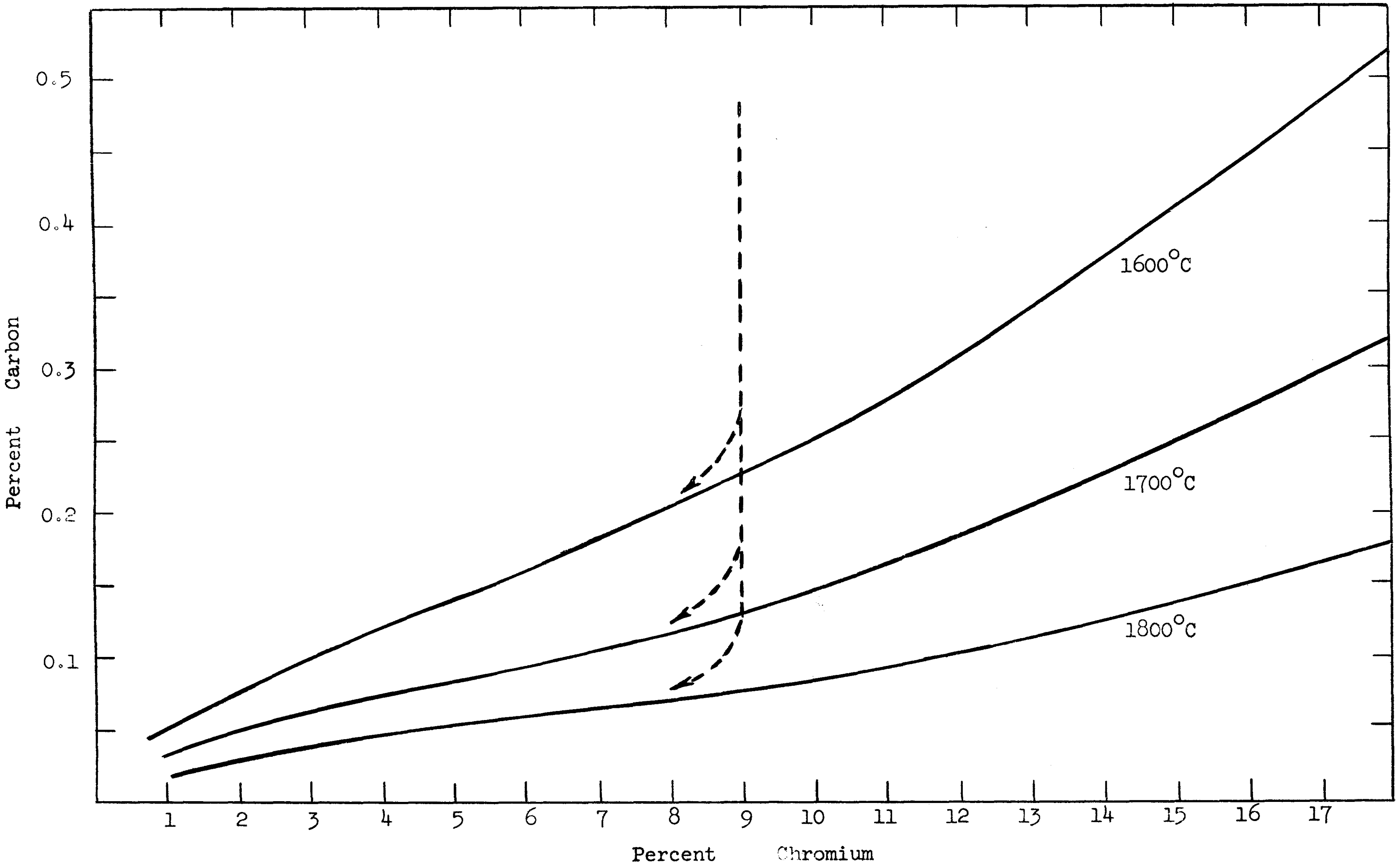

FIG. 1 CARBON - CHROMIUM RELATIONSHIP IN LIQUID IRON, CO PRESSURE 1 ATM.

III. OUTLINE OF INVESTIGATION

The investigation was initiated in order to follow the changes in the carbon and chromium concentrations of iron-chromium-carbon melts during oxidation at 1600°C, conducted by the blowing of gaseous oxygen on to the slag-free metal surface. The open metal surface permitted intimate contact between the gas and metal, thus eliminating the need for high gas velocities to blow away a liquid slag cover. In the experimental oxidation by means of gas impingement on the metal, the rate of oxidation was slowed considerably, compared to that encountered in production methods. This made possible the maintenance of the melt temperature at 1600° ± 10°C. The experimental oxygen input rates did not exceed an equivalent carbon oxidation rate of 0.020 percent carbon per minute. This compares to an equivalent carbon oxidation rate of approximately 0.055 percent carbon per minute, for an oxygen blowing rate of 1000 cubic feet per ton per hour, which is common to production techniques.

1. The initial runs were conducted by blowing oxygen at varying rates on to the surface of iron-chromium-carbon melts, with a chromium concentration of approximately 10 percent, and a furnace atmosphere consisting of the gaseous product of carbon oxidation.

2. The results of the initial series of runs led to the investigation of the effect of argon dilution of the furnace atmosphere during the oxygen blow. A holding period following the oxygen blow was incorporated into the runs, to determine possible further changes in the melt composition. The holding period was introduced due to the inability to account for the total

oxygen input by means of mass balances with the carbon and chromium losses shown by the composition of the melt at the end of the oxygen blow. In calculating the mass balances, the assumption was made that the carbon oxidized to carbon monoxide and the chromium oxidized to the equilibrium oxide (Cr_3O_4).

3. The reactions between carbon and chromium in the melt and the oxide crust generated during the oxygen blow, were investigated further, during a prolonged holding period following the oxygen blow, with argon entering the furnace chamber. The continued carbon oxidation during the holding period was compared to the oxidation of carbon in the metal under chromic oxide, which was added to the melt surface.

4. The oxidation of carbon and chromium was investigated by means of air blowing on to the melt surface. This method of oxidation extended the period during which the decarburization was characterized by a continuously decreasing rate.

5. In order to maintain intimate gas-metal contact throughout the entire period of oxidation, runs were conducted by bubbling air through the iron-chromium-carbon melts.

6. The results of oxygen blowing runs demonstrated that iron was oxidized along with chromium. In order to investigate a hypothetical mechanism suggested for the oxidation of chromium in solution in liquid iron, the oxidation of a nickel melt, containing carbon and chromium in solution, was examined by bubbling air through the metal.

IV. DESCRIPTION OF APPARATUS

The experimental arrangement is shown schematically in Figure 2. The runs were conducted in an induction furnace, utilizing magnesia crucibles having an inside diameter of 3.5 inches. The stirring effect of the induction coil was considered to be advantageous in providing a melt having a homogeneous composition. The charge weight used was mainly 1200 grams, with an initial series of runs having a 1500 gram charge weight. The metal temperature was measured by the use of a noble metal thermocouple, sheathed in a recrystallized alumina protection tube which was immersed in the molten metal at all times. The furnace chamber was sealed by a water cooled copper head, having ports for viewing and sampling.

The oxidizing gas was blown on to the surface of the melt, or bubbled through the melt, through a recrystallized alumina tube, having an inside diameter of 0.125 inches. The flow rate of the oxidizing gas was controlled by means of flowmeters. A gas inlet to the furnace chamber was available, through which argon could be introduced in order to vary the furnace atmosphere.

The charge materials consisted of electrolytic iron, electrolytic chromium metal, and flake graphite. The sampling of the metal was conducted by using six millimetre vycor tubing and a squeeze bulb.

The chemical analyses conducted in this investigation involved the determination of the carbon and chromium concentrations in the metal samples. The carbon contents were determined using the Gravimetric Method for concentrations above approximately 0.04 percent. For lower carbon concentrations, the Conductometric Method was used. The accuracy of the reported concentrations

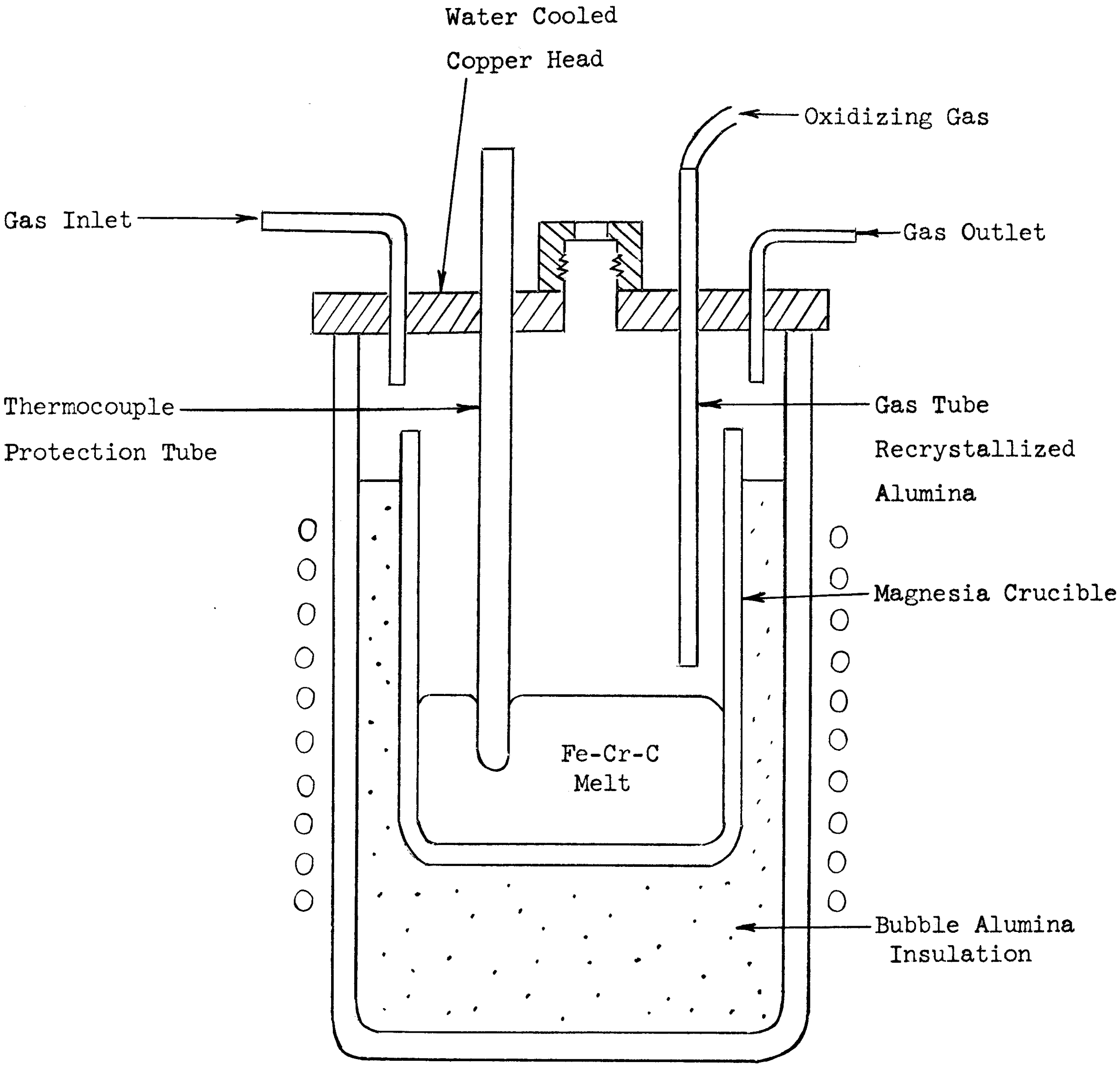

FIG. 2 DRAWING OF EXPERIMENTAL ARRANGEMENT

is considered to be ± 0.005 percent at 0.05 percent carbon, and ± 0.001 percent for carbon levels below 0.02 percent. The chromium contents were determined using the Persulphate Oxidation Method, with reported concentrations accurate to within ± 0.1 percent at levels of 20 percent chromium, and ± 0.07 percent at 10 percent chromium.

V. EXPERIMENTAL RESULTS

The procedure that characterized the initial series of runs involved the blowing of oxygen continuously on to the metal surface, with sampling of the metal conducted periodically during oxidation. The melt surface was open to the furnace atmosphere with no slag cover. The initial carbon and chromium concentrations in the metal were such that the melt composition was well away from the equilibrium indicated by the carbon-chromium relationships shown in Figure 1. It was desired to observe the path followed by the carbon and chromium concentrations during the approach to equilibrium. The rate of oxygen input was varied, with flow rates of 120, 200, and 250 millitres per minute (S.T.P.). The furnace atmosphere consisted of the gaseous products of oxidation.

Observation of the metal surface during the course of the runs, provided visual evidence of three stages:

1. Initially, the appearance of the metal surface gave no evidence of reactions occurring. No indication of "boiling", such as would be expected with gas bubbles rising through the metal, was observed.

2. The first visual evidence of reaction was the appearance of bright oxide flashes which radiated from the gas-metal impingement area, directly beneath the gas tube. The oxide that appeared in these flashes was not retained but disappeared rapidly.

3. The third stage observed was characterized by the formation of a stable oxide island beneath the gas tube. This island grew in size, while dark patches appeared within it. The island growth continued until the surface

of the metal was covered by a crusty, solid oxide.

In Figure 3, analyses for the samples taken during oxidation have been plotted to illustrate the path followed by the metal composition during oxidation. It is evident that, in each case, the carbon oxidized preferentially, with no loss of chromium, during the initial vertical approach to the equilibrium line. The initiation of chromium loss, which is shown by the departure from a vertical path, occurred at higher levels of carbon concentration with increased rate of oxygen input. Noteworthy is the fact that penetration of the 1600°C equilibrium line occurred, with final melt composition lying in the range between the equilibrium indicated for 1600°C and 1700°C, with a pressure of carbon monoxide of one atmosphere.

Figure 4 illustrates the rate of carbon and chromium oxidation experienced in these runs. It will be noted for each individual run, the initial rate of carbon loss was constant, providing a straight line relationship between carbon concentration and time of oxidation. Departure from the straight line relationship occurred at higher levels of carbon concentration as the rate of oxygen input increased. As the carbon oxidation rate deviated from a straight line relationship, the oxidation of chromium commenced. Comparing the three rates of oxygen input, an unexpected occurrence is indicated by the chromium loss rate. The rate of chromium oxidation shows no apparent increase with increased rate of oxygen input. The data indicate a constant rate of chromium loss of approximately 0.02 percent chromium per minute for the three rates of oxygen input.

The significant points that emerged from these runs may be summarized:

1. The oxidation of carbon occurred at the gas-metal interface, with

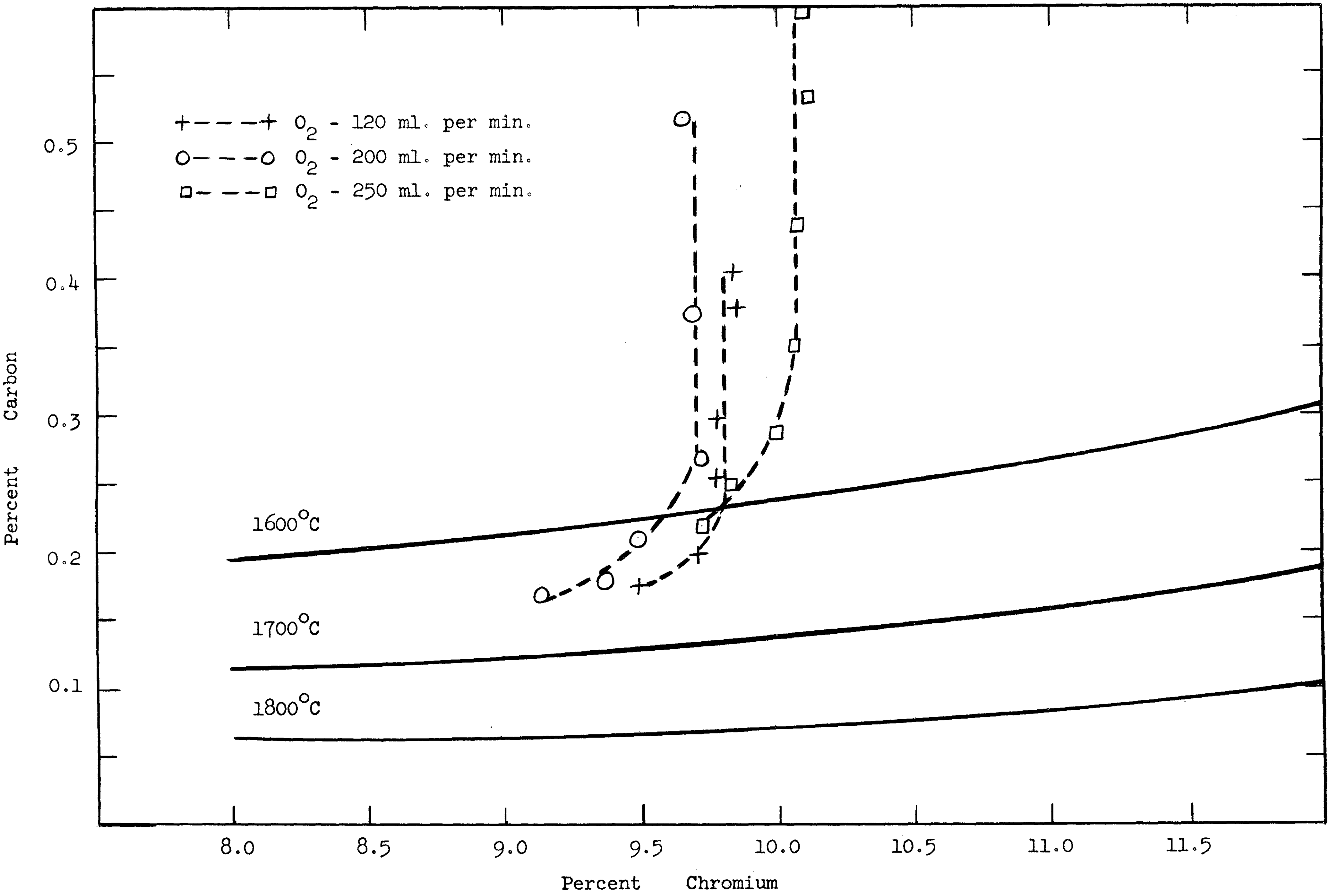

FIG. 3 C-Cr RELATIONSHIPS - OXYGEN BLOWING, FURNACE ATMOSPHERE CO

no indication of the formation of carbon monoxide bubbles at the metal-refractory interface. This is similar to the evidence reported by Fujii[4,5,6] in studying the oxidation of carbon in iron under oxygen-argon gas mixtures.

2. The initial oxidation of carbon occurred at a constant rate, with no evidence of carbon diffusion in the metal controlling the oxidation rate during this stage. A constant decarburization rate was reported by Fujii, and also by Baker, Warner, and Jenkins[7] in levitation experiments.

3. A point was reached where the decarburization rate was no longer constant. This has also been reported by Fujii, with the interpretation that the control of the rate of carbon oxidation was then by carbon diffusion in the metal. Baker, Warner, and Jenkins did not encounter this change in carbon oxidation rate at the carbon levels at which their experiments terminated.

4. During the stage of the constant decarburization rate, no loss of chromium was experienced. When the rate of carbon oxidation decreased, the oxidation of chromium was initiated. The rate of chromium loss was, however, independent of the rate of oxygen input.

5. The equilibrium line indicated by the carbon-chromium relationships at 1600°C and one atmosphere pressure of carbon monoxide, was penetrated in each of the experimental runs.

Table I provides mass balances taken for the period from the start of oxygen input to the point where the constant rate of carbon oxidation terminated. The oxygen input is compared to the carbon loss as carbon monoxide.

From the balances shown in Table I, during the constant rate of carbon oxidation, the reaction may be expressed by the chemical equation:

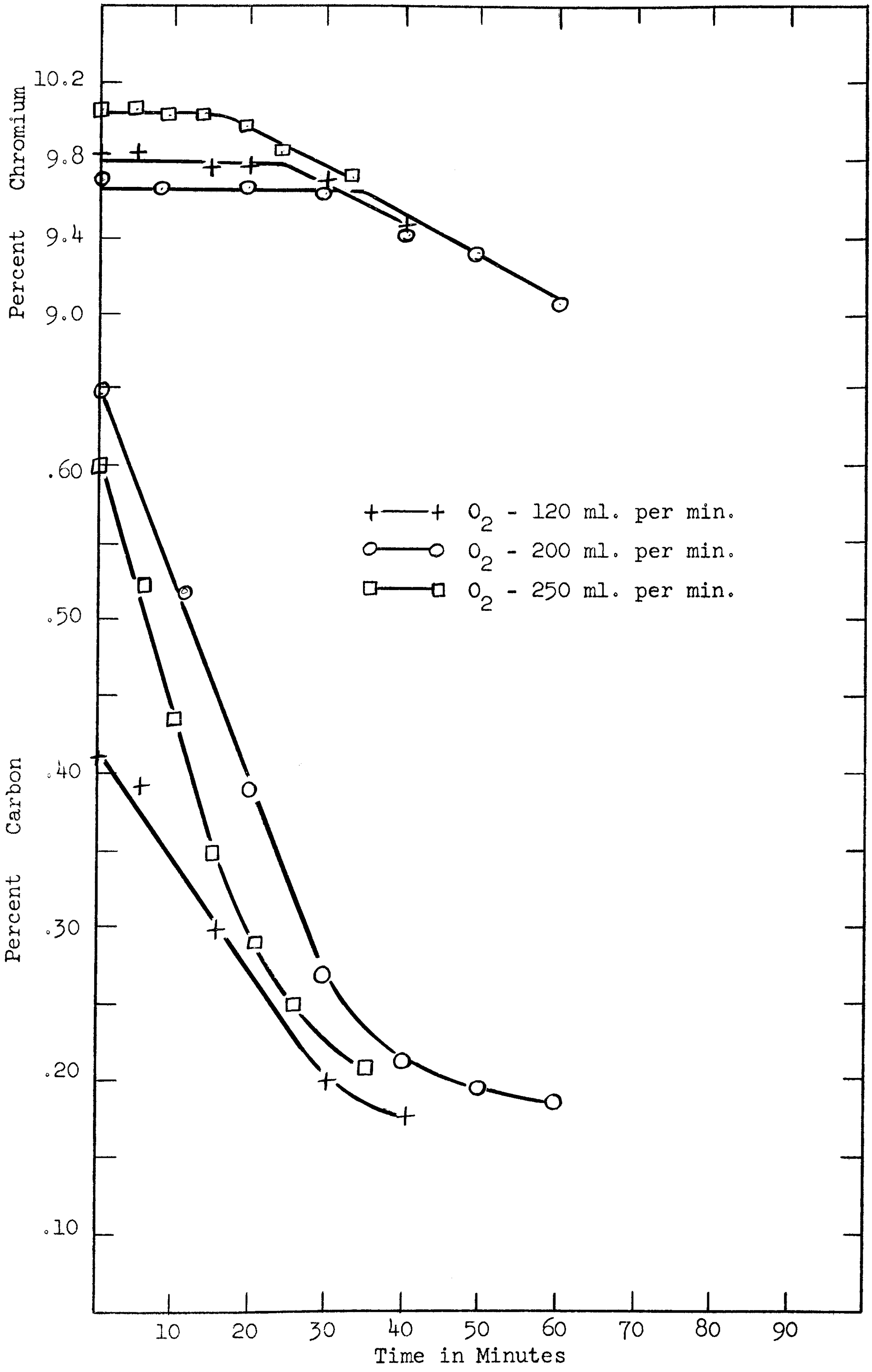

FIG. 4 CARBON AND CHROMIUM OXIDATION RATES

$$\underline{C} + 1/2\ O_2(g) = CO(g).$$

Oxidation of carbon monoxide to carbon dioxide to any appreciable extent is not indicated by the oxygen balances.

Table II presents oxygen balances, taken over the complete duration of the runs, considering the generation of carbon monoxide and formation of Cr_3O_4, which is the equilibrium oxide of chromium for the chromium concentrations involved.

It is evident from the balances shown in Table II, that the formation of carbon monoxide and Cr_3O_4 does not account for the total oxygen input. The possibility of carbon dioxide formation does not appear to be a likely means of additional oxygen consumption, in view of the indication from the balances shown in Table I, that carbon dioxide formation is not involved to any appreciable extent during the initial carbon drop. Formation of metallic oxide other than Cr_3O_4, beyond the point of termination of the constant rate of carbon oxidation is likely.

With regard to the point of termination of the initial constant rate of decarburization, it was shown that the carbon concentration at this point increases with increased rate of oxygen input. It may be postulated that this trend would continue in such a manner that with high oxygen blowing rates, the initial constant rate of carbon loss would be suppressed entirely and chromium oxidation would be experienced initially along with carbon oxidation.

With a slag covering the metal initially, intimate gas-metal contact

TABLE I

Mass Balances - Oxygen Input vs. Carbon Loss as CO During Initial Constant Decarburization Rate

Oxygen Input Rate	Percent Carbon		Time in	Carbon Loss	Oxygen Input	Moles O_2 Required
Ml. per Min.(S.T.P.)	Initial	Final	Minutes	Gram Moles	in Moles	as CO (g)
120	0.41	0.21	25	0.25	0.13	0.125
200	0.65	0.28	28	0.47	0.25	0.24
250	0.60	0.35	15	0.32	0.16	0.16

TABLE II

Mass Balances - Total Oxygen Input vs. Carbon and Chromium Losses as CO and Cr_3O_4.

Oxygen Input Rate	Oxygen Input	Carbon Loss	Chromium Loss	Moles O_2 As		
Ml. per Min.(S.T.P.)	in Moles	Gram Moles	Gram Moles	CO	Cr_3O_4	Total
120	0.214	0.288	0.098	0.144	0.065	0.209
200	0.535	0.59	0.18	0.30	0.12	0.42
250	0.390	0.49	0.09	0.25	0.06	0.31

would depend on the velocity of the oxygen stream being sufficient to blow away the slag at the impingement area. Carbon monoxide formation, other than at this impingement area, would no doubt involve the refractory-metal interface.

In view of the evidence that the carbon-oxygen reaction occurred at the gas-metal interface in the present experimental runs, it was of interest to determine the effect of dilution of the furnace atmosphere by means of argon, during oxidation. Carbon oxidation would be expected to proceed to lower carbon concentrations if the partial pressure of carbon monoxide at the gas-metal interface was lowered by argon dilution. Also, the evidence that carbon monoxide and Cr_3O_4 formation has not accounted for the entire oxygen input requires further consideration.

Oxygen Blowing with Furnace Atmosphere Diluted by Argon

In this series of experimental runs, oxygen blowing was conducted at input rates of 100, 150, and 225 millitres per minute (S.T.P.), with argon passing through the furnace chamber. The initial chromium concentration was approximately 10 percent. One run was conducted with an initial chromium content of 15 percent, and an oxygen blowing rate of 100 millitres per minute.

Visual observations of the metal surface during the oxygen blow were similar to those for the initial series of runs. The metal surface was completely covered by a solid oxide crust during oxygen blowing. Following the termination of the oxygen blow, the melt was held at 1600°C, while continuing the flow of argon through the furnace chamber. Metal samples were

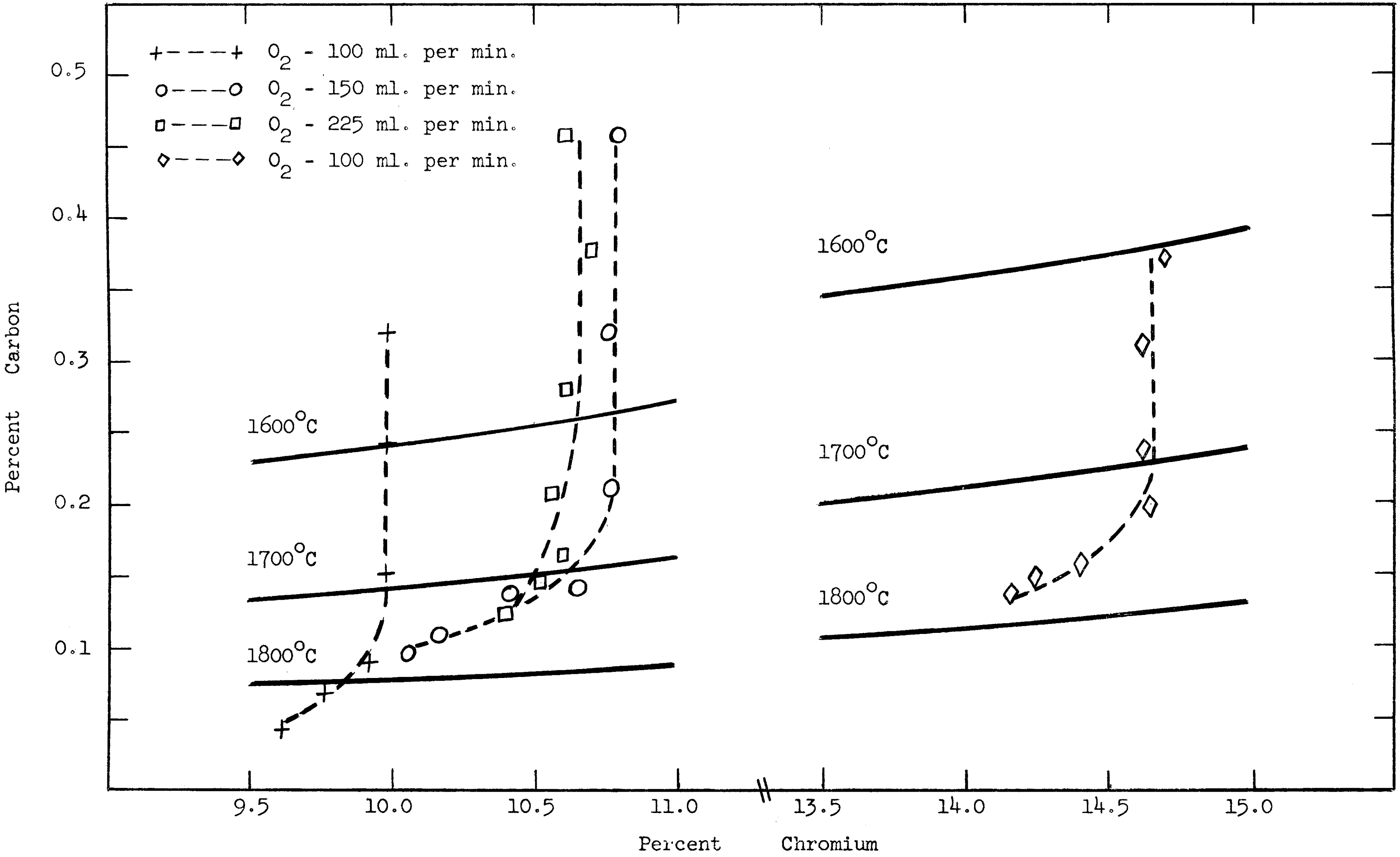

FIG. 5 C-Cr RELATIONSHIPS, OXYGEN BLOWING, p_{CO} IN FURNACE LESS THAN 1 ATMOSPHERE

taken periodically during the oxygen blowing period and the holding period that followed. During the holding period, the oxide crust diminished in size, while open metal reappeared.

Figure 5 shows the carbon-chromium relationships that were obtained in these runs. The 1600°C equilibrium line (p_{CO} = 1 atmosphere) was penetrated to a greater extent than had occurred in the initial series of runs. This indicates that the partial pressure of carbon monoxide at the gas-metal interface had indeed been lowered by the introduction of argon into the furnace atmosphere. The initial vertical drop, illustrating preferential carbon oxidation, is again evident, with a deviation from this vertical path as chromium oxidation commenced.

Figure 6 illustrates the rates of carbon and chromium oxidation experienced in these runs. Similar to the observations in the previous series of runs, an initial constant rate of carbon oxidation was evident for each run. The carbon loss deviated from this constant rate with the commencement of chromium oxidation. A constant rate of chromium loss, independent of the rate of oxygen input, was again evident.

The point at which oxygen blowing was terminated is indicated by the small arrows in Figure 6. To be noted is the fact that, during the holding period that followed the end of the oxygen blow, the loss of both carbon and chromium continued.

Table III presents oxygen balances taken between the start of oxidation and the point of termination of the constant rate of decarburization. Similar to the evidence shown by the previous series of runs, the oxygen balances in Table III do not indicate carbon dioxide formation during the initial carbon

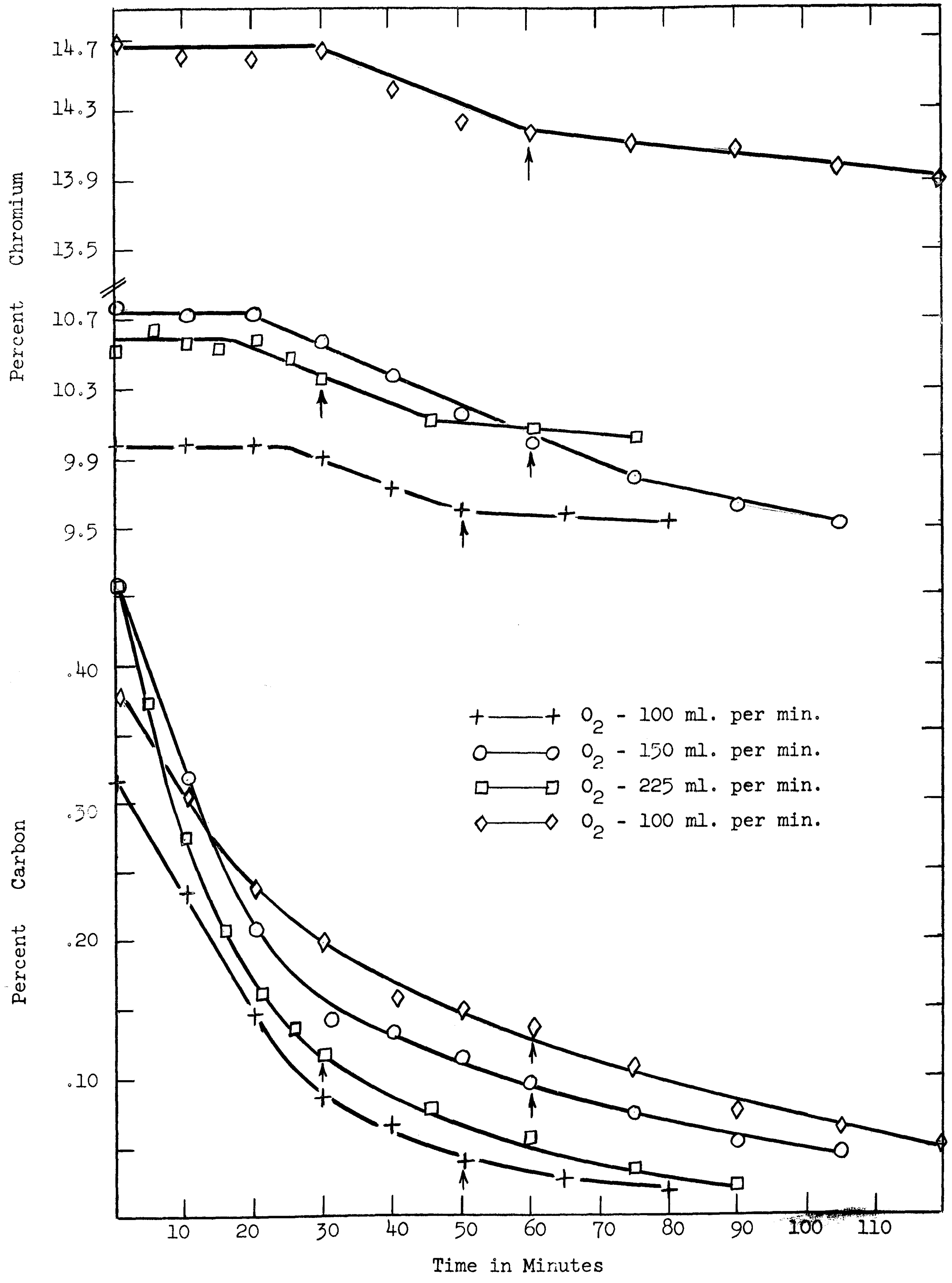

FIG. 6 CARBON AND CHROMIUM OXIDATION RATES

oxidation. The decarburization reaction may be expressed by the equation:

$$\underline{C} + 1/2\ O_2\ (g) = CO\ (g).$$

Table IV presents oxygen balances taken between the start of oxidation and the point where the oxygen blow was terminated. Similar to the observation in the previous series of runs, the oxygen balances at the end of oxygen blowing fail to account for the entire oxygen input in terms of the formation of carbon monoxide and Cr_3O_4.

Table V shows oxygen balances taken over the entire duration of the runs, including the holding period that followed the oxygen blow. The data shown in Table V indicate a good balance between the total oxygen input and the total formation of carbon monoxide and Cr_3O_4 over the entire duration of the runs. This suggests that, at the stage represented in Table IV at the end of the oxygen blow, the oxygen introduced has reacted to form carbon monoxide, chromium oxide, and an additional oxide that has subsequently reacted with carbon and chromium during the holding period, to form additional carbon monoxide and chromium oxide. This additonal oxide formed during the oxygen blow must be iron oxide, and the reactions taking place during the holding period may be represented:

$$4\ FeO(l) + 3\ \underline{Cr} = Cr_3O_4(s) + 4\ Fe(l).$$

$$FeO(l) + \underline{C} = Fe(l) + CO(g).$$

The significant points from this series of runs may be summarized:

TABLE III

Mass Balances - Oxygen Input vs. Carbon Loss as CO During Initial Constant Decarburization Rate - Argon Passing Through Furnace Chamber.

Oxygen Input Rate	Percent Carbon		Time in	Carbon Loss	Oxygen Input	Moles O_2 Required
Ml. per Min.(S.T.P.)	Initial	Final	Minutes	Gram Moles	in Moles	as CO (g)
100	0.32	0.15	20	0.17	0.089	0.085
150	0.46	0.24	16	0.22	0.107	0.11
225	0.46	0.32	6	0.14	0.06	0.07
100	0.38	0.24	18	0.14	0.08	0.07

TABLE IV

Mass Balances - Total Oxygen Input vs. Carbon and Chromium Losses as CO and Cr_3O_4 During the Oxygen Blow - Argon Passing Through Furnace Chamber.

Oxygen Input Rate	Oxygen Input	Carbon Loss	Chromium Loss	Moles O_2 As		
Ml. per Min.(S.T.P.)	in Moles	Gram Moles	Gram Moles	CO	Cr_3O_4	Total
100	0.223	0.28	0.085	0.14	0.057	0.197
150	0.402	0.36	0.171	0.18	0.114	0.294
225	0.301	0.34	0.039	0.17	0.026	0.196
100	0.268	0.24	0.12	0.12	0.08	0.20

TABLE V

Mass Balances - Oxygen Input vs. Carbon and Chromium Losses as CO and Cr_3O_4 During the Oxygen Blow and Holding Period - Argon Passing Through Furnace Chamber.

Oxygen Input Rate	Oxygen Input	Carbon Loss	Chromium Loss	Moles O_2 As		
Ml. per Min.(S.T.P.)	in Moles	Gram Moles	Gram Moles	CO	Cr_3O_4	Total
100	0.223	0.30	0.095	0.15	0.065	0.215
150	0.402	0.41	0.283	0.205	0.19	0.395
225	0.301	0.43	0.122	0.215	0.082	0.297
100	0.268	0.33	0.178	0.165	0.110	0.275

1. The introduction of argon into the furnace atmosphere lowered the partial pressure of carbon monoxide at the gas-metal interface. This resulted in a drop in carbon concentration to levels well below that indicated by the equilibrium carbon-chromium relationships for 1600°C and one atmosphere pressure of carbon monoxide.

2. Oxidation of carbon initially occurred at a constant rate, consuming all of the oxygen introduced by the formation of carbon monoxide.

3. Deviation of the carbon oxidation from a constant rate occurred at higher carbon concentrations as the rate of oxygen input increased. With a chromium concentration of 15 percent, the carbon concentration at the end of the constant decarburization rate, also increased over that observed at the 10 percent chromium content, for the same rate of oxygen input.

4. Beyond the stage of the constant decarburization rate, the formation of carbon monoxide and Cr_3O_4 does not account for the total oxygen input.

5. During the holding period following the end of oxygen blowing, both carbon and chromium continued to oxidize. It is presumed that iron oxide formed along with chromium oxide as the rate of carbon loss declined, and that this iron oxide subsequently reacted with carbon and chromium in the metal, as shown by their continuing loss.

Figure 7 shows a plot of the initial constant decarburization rate in moles carbon per minute, against oxygen blowing rate in moles per minute, for the experimental runs of the first two series. The straight line indicates the relationship expected by the reaction:

$$\underline{C} + 1/2\, O_2\ (g) = CO\ (g),$$

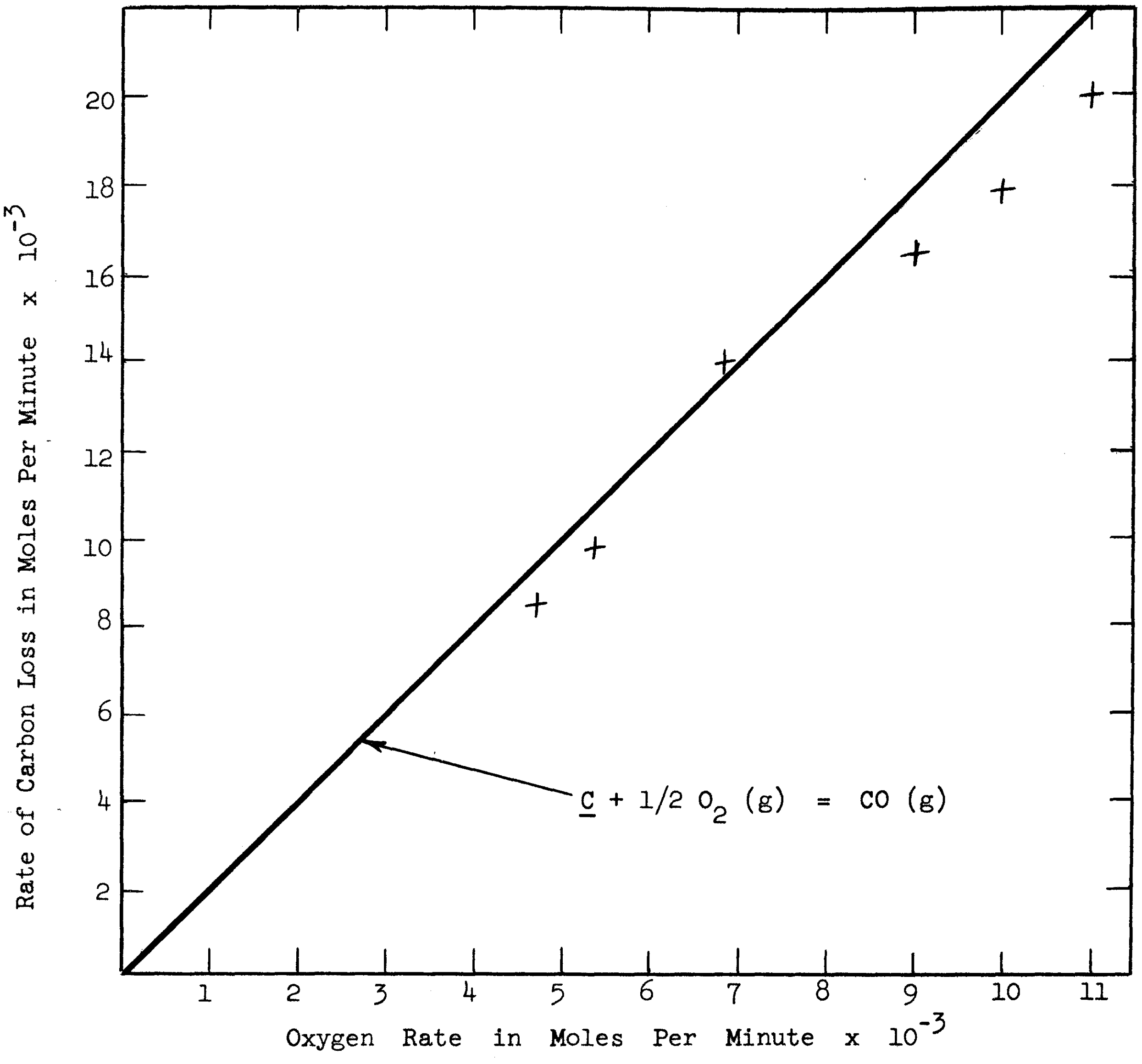

FIG. 7 CONSTANT DECARBURIZATION RATE VS. OXYGEN INPUT RATE

and is not drawn to fit the experimental points. It will be noted that the agreement between the experimental points and the theoretical line is quite good. The tendency of the experimental points to a slightly greater departure from the line at the higher oxygen rates could be interpreted as an indication of carbon dioxide formation. However, in view of the difficulty in reading slopes from the carbon oxidation rate plots, it is probable that this deviation is due to lack of precision in the data. It is therefore assumed that the initial carbon oxidation reaction occurring in the experimental runs is represented by the above chemical equation.

Carbon Oxidation by Reduction of Chromium Oxide with Furnace Atmosphere Diluted by Argon

The continuation of both carbon and chromium oxidation, during the holding period following oxygen blowing, that was experienced in the previous series of runs, suggested that this process should be examined more closely. A run was conducted in which oxygen was blown continuously for a period of fifty minutes at a rate of 120 millitres per minute. The furnace head was not opened for sampling the metal, until the oxygen blow was terminated. At the end of the oxygen blow, visual examination showed the surface of the metal to be covered by a solid oxide crust. The furnace atmosphere, during the oxygen blow, consisted of the gaseous product of carbon oxidation.

Immediately following the sampling of the metal at the end of oxygen blowing, argon was passed through the furnace chamber, with metal samples taken periodically during a holding period of one hour. During the holding

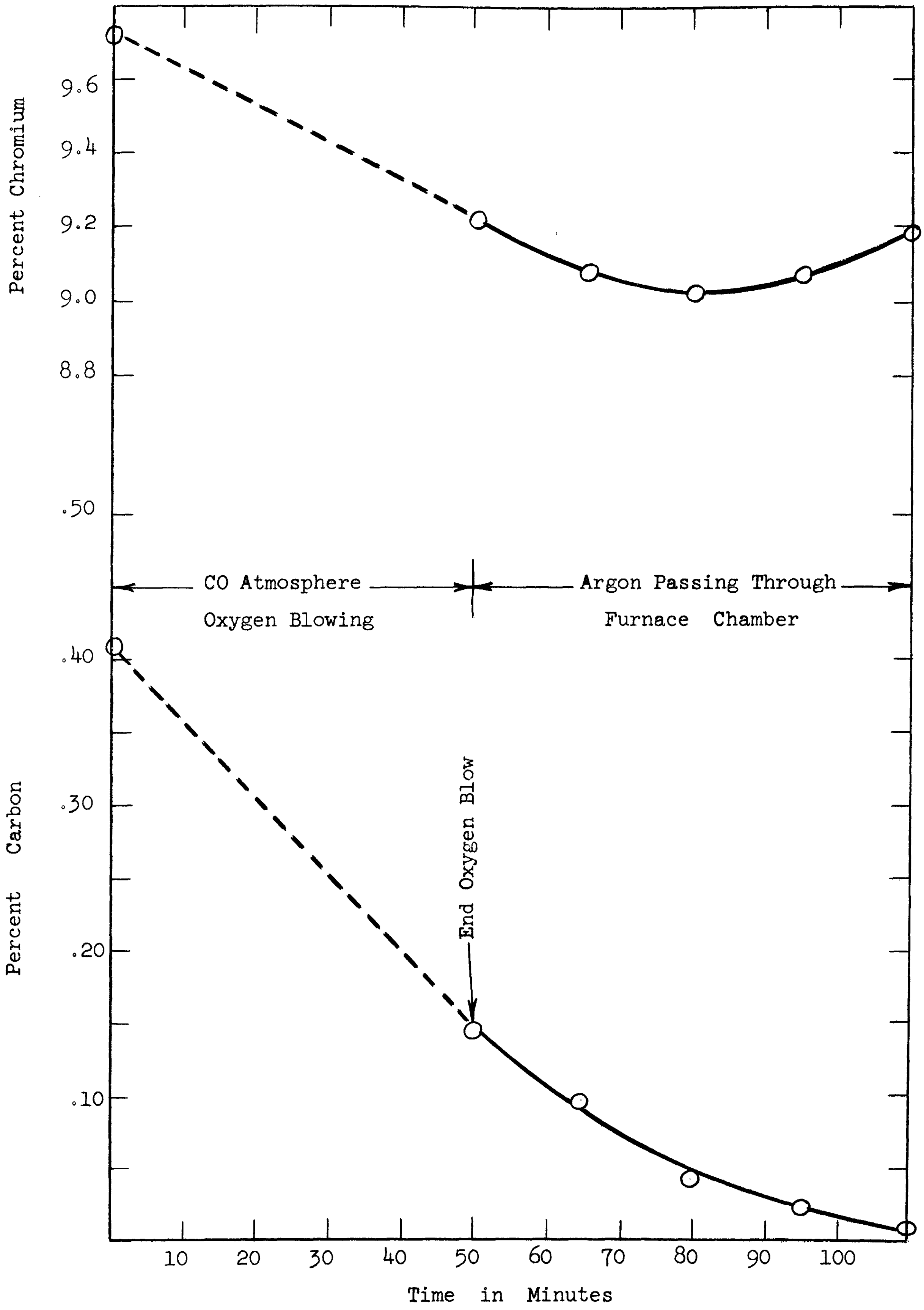

FIG. 8 CARBON OXIDATION RATE - HELD UNDER OXIDE GENERATED DURING OXYGEN BLOW

period, the oxide crust diminished considerably in size, while the open metal surface reappeared.

Figure 8 illustrates the results obtained in this run. During the oxygen blow, carbon oxidized from an initial concentration of 0.41 percent to 0.15 percent. The chromium content fell from an initial 9.72 percent to 9.22 percent. During the holding period, carbon continued to oxidize, reaching a concentration of 0.01 percent at the end of the holding period. The chromium concentration reached a minimum of 9.02 percent during the first 30 minutes of holding, then increased to a final concentration of 9.18 percent at the end of the holding period.

Table VI presents mass balances between the input of oxygen and the carbon monoxide and Cr_3O_4 formed. Calculations for the balances were based on the carbon and chromium losses at the end of the oxygen blow and over the entire duration of the run.

TABLE VI

Mass Balances - Total Oxygen Input vs. Carbon and Chromium Losses as CO and Cr_3O_4: (a) During Oxygen Blow; (b) Including Holding Period.

Oxygen Input in Moles	Period of Oxygen Blow Moles O_2 as			Entire Duration of Run Moles O_2 as		
	CO	Cr_3O_4	Total	CO	Cr_3O_4	Total
0.27	0.13	0.075	0.205	0.20	0.08	0.28

These data confirm the evidence presented by the previous series of runs, that the continued oxidation of carbon and chromium is due to reactions between these two elements and iron oxide that formed during the oxygen blow. These reactions were represented by the chemical equations:

$$\mathrm{FeO\ (l)} + \underline{\mathrm{C}} = \mathrm{Fe\ (l)} + \mathrm{CO\ (g)}$$

$$3\underline{\mathrm{Cr}} + 4\mathrm{FeO\ (l)} = \mathrm{Cr_3O_4\ (s)} + 4\mathrm{Fe(l)}.$$

In addition to these reactions, which occurred during the first half of the holding period, reduction of chromium oxide by carbon in the melt occurred during the balance of the holding period, resulting in an increase in chromium concentration. This may be represented by the chemical equation:

$$\mathrm{Cr_3O_4\ (s)} + 4\ \underline{\mathrm{C}} = 3\underline{\mathrm{Cr}} + 4\mathrm{CO\ (g)}.$$

This latter reaction was probably activated by the low partial pressure of carbon monoxide at the open metal surface, due to the effect of the argon flow.

In view of this latter occurrence, a run was conducted in an attempt to duplicate the process. The initial composition of the melt was 0.20 percent carbon and 10.73 percent chromium. Added to the surface of the melt was 0.2 gram moles of chromic oxide (Cr_2O_3). Argon was passed through the furnace chamber while the melt was held at 1600°C, with periodic sampling of the metal during a holding period of 80 minutes. Figure 9 shows the results obtained in this run. The carbon content fell from the initial 0.20 percent to a final concentration of 0.005 percent, while the chromium concentration increased from 10.73 to 11.06 percent.

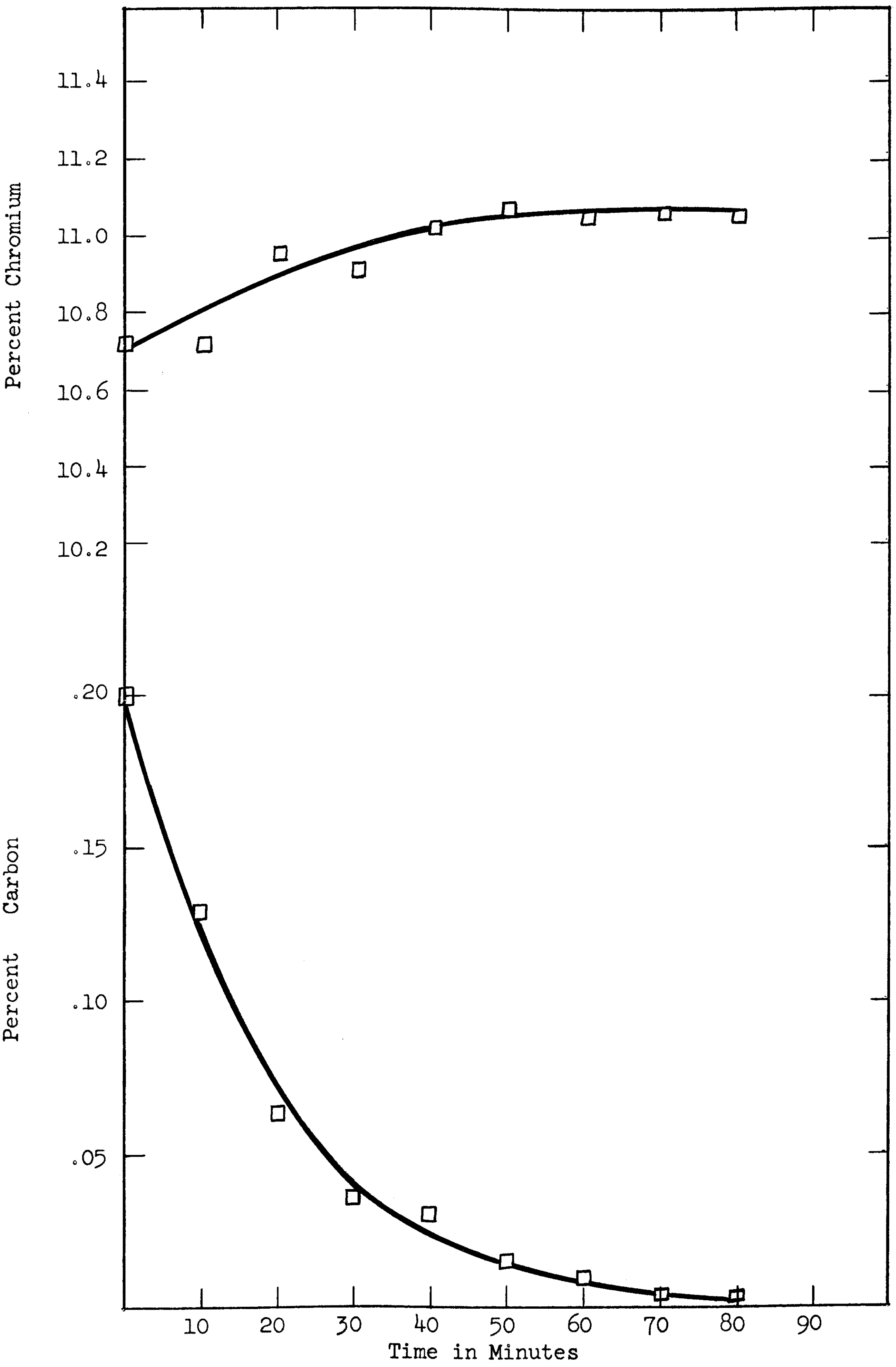

FIG. 9 CARBON OXIDATION RATE - HELD UNDER CHROMIC OXIDE

In Figure 10, the negative logarithm of carbon concentration is plotted against the holding time for the above two runs. A straight line relationship is indicated by these data, with an approximate slope (-d log % C/dt) equal to 2.0×10^{-2}.

The straight line relationship, shown by these data, suggests that control of the rate of carbon oxidation may be considered to be the diffusion of carbon in the metal to the metal surface where direct oxidation takes place.

In considering the absorption of gases in water, Whitman and coworkers[15,16,17] suggested that the rate of absorption is limited by processes of diffusion. The hypothesis stated that whenever a liquid and a gas come into contact, there exists on either side of the interface a surface layer of gas and of liquid which is practically free from mixing by convection. This "two-film" theory is expressed by assuming the existence of stationary boundary layers of gas and liquid on the two sides of the interface. In the main body of the gas or liquid, mixing by convection is sufficiently rapid that the concentration of solute in the fluid is essentially uniform. Transfer of solute through the films is effected by the relatively slow process of diffusion. Diffusion through the gas film proceeds at a rate proportional to the differential in solute concentrations in the bulk gas and at the interface. Diffusion through the liquid film is controlled by the difference in concentration of the solute in the liquid at the interface and the solute concentration in the bulk liquid.

Under certain circumstances, the resistance of one of the films may be so much greater than that of the other that the second film may be neglec-

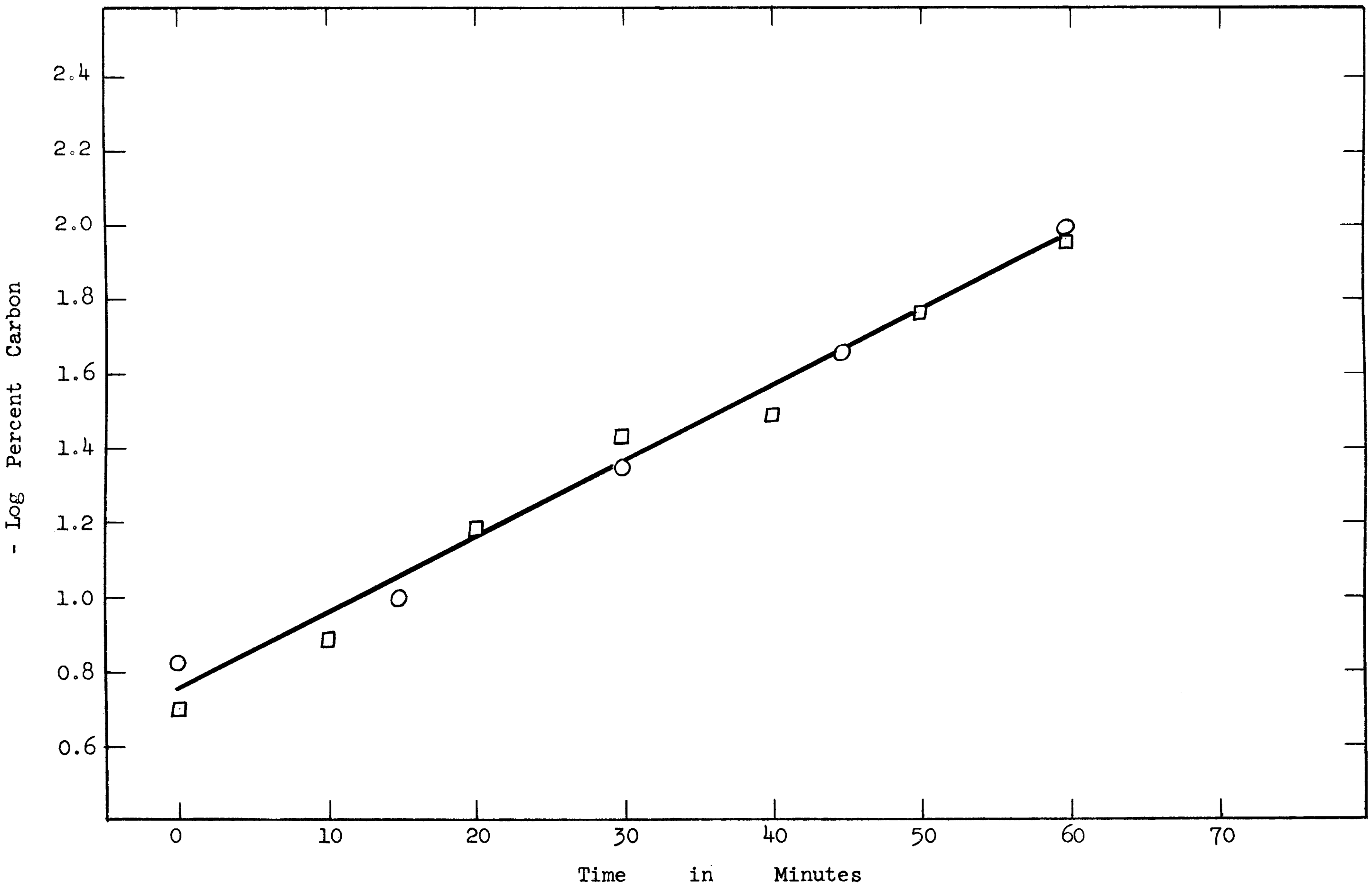

FIG. 10 RELATIONSHIP BETWEEN LOG CARBON CONCENTRATION AND HOLDING TIME UNDER CHROMIUM OXIDE

ted and the problem treated as if only one film existed. Because of the greater density of the liquid, the collisions in the liquid are much more frequent and the diffusional resistance is consequently greater than in the gas.

Higbie[18] investigated the rate of absorption of pure gas in water, considering the liquid film as rate-controlling.

Darken[19] suggested the application of the diffusion film or boundary layer theory to the consideration of the carbon boil in the open hearth furnace. His treatment involved the assumption that oxygen from the slag diffuses through a thin layer or film of metal, and is mixed by convection beyond this film.

Application of the "two-film" or boundary layer hypothesis has also been presented by King,[20] in analysing the carbon boil in steelmaking. By considering the virtual maximum rates of the several steps in the mechanism of carbon oxidation, it was shown that the possible controlling steps for the rate of decarburization were:

(a) transport of iron in the slag to the slag-metal phase boundary.

(b) transport of oxygen in the metal, away from the slag-metal phase boundary.

(c) transport of oxygen and carbon in the metal, from the bulk metal to the phase boundary between metal and carbon monoxide bubbles.

Rates of solute transfer through the hypothetical films or boundary layers are estimated from the relationship:

$$j_i = \frac{-D_i \, (C_i^{'} - C_i^{*})}{\delta_i} \qquad (1)$$

j_i = flux of component i in moles per square centimetre per second.

D_i = diffusity of component i in the solvent, in square centimetres per second.

C_i^* = concentration of component i at the reaction interface in moles per cubic centimetre.

C_i' = concentration of component i in the bulk phase away from the interface, in moles per cubic centimetre.

δ_i = effective diffusion boundary layer thickness in centimetres, which is a function of the Reynold's and Schmidt Numbers for flow in the bulk.

The above expression may be rewritten in terms of the percentage loss of component i in the bulk liquid, as a result of diffusion to the reaction interface:

$$\frac{-d\,\%\,i}{dt} = \frac{A \cdot D_i'}{V \cdot \delta_i} (\%\,i' - \%\,i^*) \qquad (2)$$

$\frac{-d\,\%\,i}{dt}$ = loss of component i from the bulk in percent per second.

A = area of reaction interface in square centimetres.

V = volume of the bulk liquid in cubic centimetres.

$\%\,i'$ = percentage of component i dissolved in the bulk liquid.

$\%\,i^*$ = percentage of component i in the liquid at the interface.

In considering the experimental oxidation of carbon in iron containing chromium, under a chromic oxide layer such as that which existed in the run shown in Figure 9, it was suggested that control of the rate of carbon oxidation may be considered to be the diffusion of carbon in the metal to the reaction interface. It may be postulated that a thin film or boundary layer is present, such that a concentration gradient exists between the bulk carbon content and the carbon concentration at the interface. The rate of carbon loss from the bulk metal may be expressed:

$$\frac{-d\,\%\,C}{dt} = \frac{A \cdot D_C^{Fe-Cr}}{V \cdot \delta_C} \left(\%\,C' - \%\,C^*\right) \qquad (3)$$

where D_C^{Fe-Cr} = diffusivity of carbon in iron-chromium-carbon solutions.

Integration of this expression, between the initial and final carbon concentrations and from zero to time t, provides the following relationship:

$$\log \left(\frac{\%\,C^i - \%\,C^*}{\%\,C^f - \%\,C^*}\right) = \frac{A \cdot D_C^{Fe-Cr} \cdot t}{2.303\ V \cdot \delta_C} \qquad (4)$$

where $\%\,C^i$ = initial carbon concentration in the bulk metal.

$\%\,C^f$ = final carbon concentration in the bulk metal.

t = time in seconds.

During the carbon oxidation, the area of the reaction interface (A), the volume of the melt (V), the diffusivity of carbon in the melt (D_C^{Fe-Cr}), and the effective boundary layer thickness (δ_C), may be considered constant. From the very low carbon concentration reached at the end of the holding period, it may be presumed that the interfacial carbon concentration ($\%\,C^*$) is very small, and may be taken to be essentially zero. Equation (4) may be therefore rewritten:

$$\log \frac{\%\,C^i}{\%\,C^f} = k\,t \qquad (5)$$

Considering the straight line relationship shown in Figure 10, the constant (k) in the above equation may be estimated, with time expressed in seconds,

$$k = \frac{A \cdot D_C^{Fe-Cr}}{2.303 \; V \cdot \delta_C} = 3.34 \times 10^{-4}.$$

By assuming the area of the reaction interface to be the surface area of the melt, the mass transfer coefficient may be evaluated:

$$\frac{D_C^{Fe-Cr}}{\delta_C} = 2.12 \times 10^{-3}.$$

The value of the mass transfer coefficient shown above is approximately one order of magnitude smaller than King's[20] estimate of the mass transfer coefficient for carbon in the melt at the gas-metal interface during the open hearth boil. The difference in value may be due to the effect of induction stirring on the effective boundary layer thickness, the assumption that the area of the reaction interface is the surface area of the melt, and also the assumption that the interfacial carbon concentration is constant at a very low percentage.

Attention should be given to the consideration that it is the difference in chemical potential that provides the driving force for diffusion and not the actual concentration. Elliott, Gleiser, and Ramakrishna[21] discussed this consideration and suggested that the measured diffusivity for a component in a non-ideal solution may be modified:

$$D_i^a = D_i / \left(\gamma_i + C_i \frac{\partial \gamma_i}{\partial C_i} \right)$$

where D_i^a = modified diffusivity of component i.

D_i = measured diffusivity of component i.

γ_i = activity coefficient of component i at infinite dilution.

$\frac{\partial \gamma_i}{\partial C_i}$ = change in activity coefficient of component i with change in concentration of component i.

Considering the diffusion of carbon in iron-chromium-carbon solutions, the flux of carbon through the hypothetical boundary layer may be represented by:

$$j_C = \frac{-D_C^{Fe-Cr}}{\delta_C \cdot \gamma_C^{Cr}} \left(C_C' \cdot \gamma_C^{Cr} - C_C^* \cdot \gamma_C^{Cr} \right) \qquad (6)$$

where γ_C^{Cr} = activity coefficient of carbon due to the influence of chromium (assumed constant over small changes in chromium concentration).

Based on the consideration that the driving force for diffusion is the chemical potential, the diffusivity of carbon in iron-chromium-carbon solutions may be related to the measured diffusivity of carbon in iron-carbon solutions according to:

$$D_C^{Fe-Cr} = D_C' \cdot \gamma_C^{Cr}$$

By substituting in equation (6), the following relationship is obtained:

$$j_C = \frac{-D_C' \cdot \gamma_C^{Cr}}{\delta_C} \quad (C_C' - C_C^*) \qquad (7)$$

The constant in equation (5) above, may now be rewritten:

$$k = \frac{A \cdot D_C' \cdot \gamma_C^{Cr}}{2.303 \; V \cdot \delta_C}$$

A reevaluation of the experimental mass transfer coefficient, in terms of the measured diffusivity of carbon in iron-carbon solutions, provides:

$$\frac{D_C'}{\delta_C} = 3.8 \times 10^{-3}.$$

Oxidation of Carbon and Chromium by Air Blowing.

In the oxygen blowing runs, it was shown that carbon oxidized preferentially at a constant rate during the initial stage, according to the reaction:

$$\underline{C} + 1/2 \; O_2 \; (g) = CO \; (g)$$

The point at which the constant rate of carbon oxidation terminated increased in carbon concentration as the rate of oxygen blowing increased. The carbon oxidation reaction occurred at the gas-metal interface, with no indication of carbon monoxide bubble formation below the surface at the refractory-metal interface. Dilution of the furnace atmosphere with argon allowed carbon to oxidize to lower levels than obtained with a furnace atmosphere consisting entirely of carbon monoxide.

Beyond the end of the constant rate of carbon oxidation, chromium and iron oxidation occurred, with the rate of chromium loss showing no dependence on the rate of oxygen input. Holding, following an oxygen blow, with the furnace atmosphere diluted by argon, resulted in continued oxidation of carbon and chromium. Holding under the oxide formed during the oxygen blow, and also under Cr_2O_3, with argon passing through the furnace atmosphere, suggested that the rate of carbon oxidation during this stage was controlled by the diffusion of carbon in the metal.

In order to examine further the rate of carbon loss beyond the termination of the constant decarburization rate, experimental runs were conducted utilizing air blowing at a rate of 300 millitres per minute (S.T.P.), on to melts containing 10 and 20 percent chromium in solution. Because of the experimental evidence that the oxidation of carbon involves the formation of carbon monoxide only, the partial pressure of carbon monoxide at the gas-metal interface, during the initial constant rate of carbon oxidation, would be expected to be 0.34 atmospheres. As the rate of carbon oxidation declines, the partial pressure of carbon monoxide at the interface would also be expected to decrease, if part of the oxygen reacts to form chromium and iron oxides.

Since Cr_3O_4 is the equilibrium oxide at the experimental chromium concentrations, the equilibrium percent carbon at the gas-metal interface, at the end of the constant rate of carbon loss, may be calculated, for a partial pressure of carbon monoxide of 0.34 atmospheres, from the relationship:

$$Cr_3O_4(s) + 4\underline{C} = 3\underline{Cr} + 4CO(g); \quad \log K = \frac{-43{,}270}{T} + 28.21$$

This calculation provides equilibrium carbon concentrations of 0.10 and 0.31 percent carbon for chromium concentrations of 10 and 20 percent respectively. It would be expected that the bulk carbon content at the end of the constant rate of carbon oxidation would be greater than these values.

The carbon oxidation rates obtained from the air blowing runs are shown in Figure 11. The deviation from the initial constant rate of decarburization occurred at carbon concentrations of 0.11 and 0.19 percent, for the two levels of chromium. These are indicated by the letters A and B in Figure 11. Although the carbon content is close to the theoretical for the 10 percent chromium level, a considerable difference exists in the case of the 20 percent chromium concentration. This indicates that the oxide formed at the gas-metal interface cannot be considered to be the equilibrium oxide Cr_3O_4. It is likely that the oxide initially formed at the interface is a combination of iron and chromium oxide.

During the second stage of carbon oxidation, beyond the point of termination of the constant decarburization rate, an island of oxide formed under the gas tube which gradually covered the surface of the melt. It was felt that the presence of this oxide crust, between the end of the gas tube and the metal surface, would disturb the intimate gas-metal contact that existed prior to its formation. For this reason, a series of experimental runs was conducted in which air was bubbled through the melt.

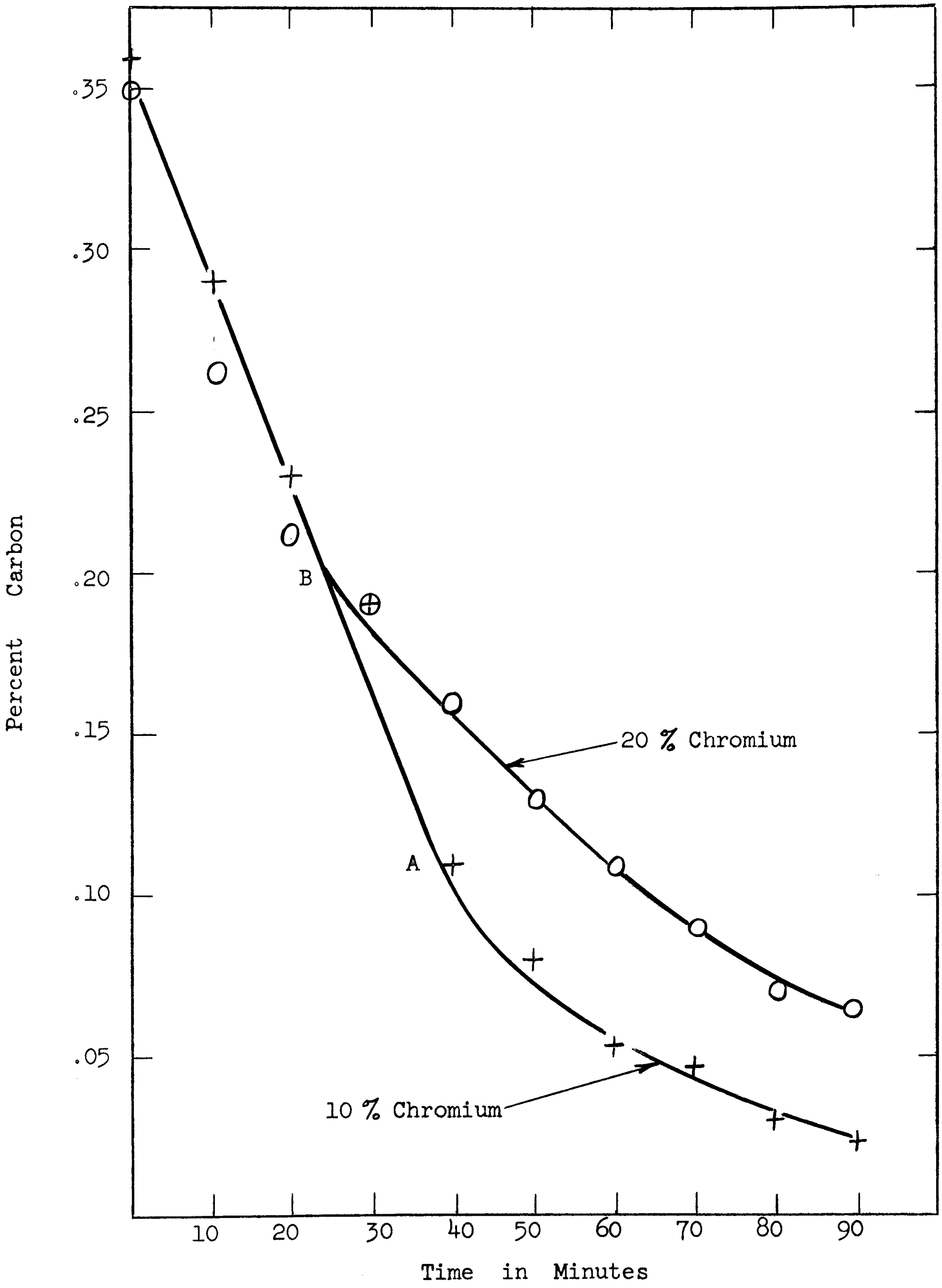

FIG. 11 CARBON OXIDATION RATES - AIR BLOWING

Oxidation of Carbon and Chromium by Air Bubbling.

Experimental runs were conducted in which air was bubbled, at a rate of 300 millitres per minute (S.T.P.), through melts containing chromium concentrations of 0, 10, 15, and 20 percent. The carbon-chromium relationships for the chromium bearing runs are shown in Figure 12.

Figure 13 presents the carbon oxidation rates for the various levels of chromium concentration, in comparison with the iron-carbon run, with no chromium present. Carbon concentrations at the end of the constant rate of carbon oxidation were 0.10, 0.14, and 0.20 percent, for the chromium levels 10, 15, and 20 percent respectively. These points are indicated by the letters A, B, and C, in Figure 13.

Figure 14 illustrates the chromium oxidation rates for the runs at 10, 15, and 20 percent chromium during air bubbling. The rate of chromium loss was similar for the three levels of chromium concentration, at approximately 0.015 percent chromium per minute. Mass balances taken between oxygen input in the air and the formation of carbon monoxide and Cr_3O_4 are shown in Table VII. The mass balances indicate that the formation of carbon monoxide and Cr_3O_4 provides a reasonable check with the oxygen input.

In Figure 15, a plot of the negative logarithm of carbon concentration, beyond the end of the constant decarburization rate, against time is shown. Similar to the observation in the oxidation of carbon by reduction of chromium oxide, the relationships may be represented by straight lines. The slopes ($-d \log \% C / dt$) are 1.86×10^{-2}, 1.07×10^{-2}, and 0.86×10^{-2} for the chromium concentrations 10, 15, and 20 percent respectively. This again

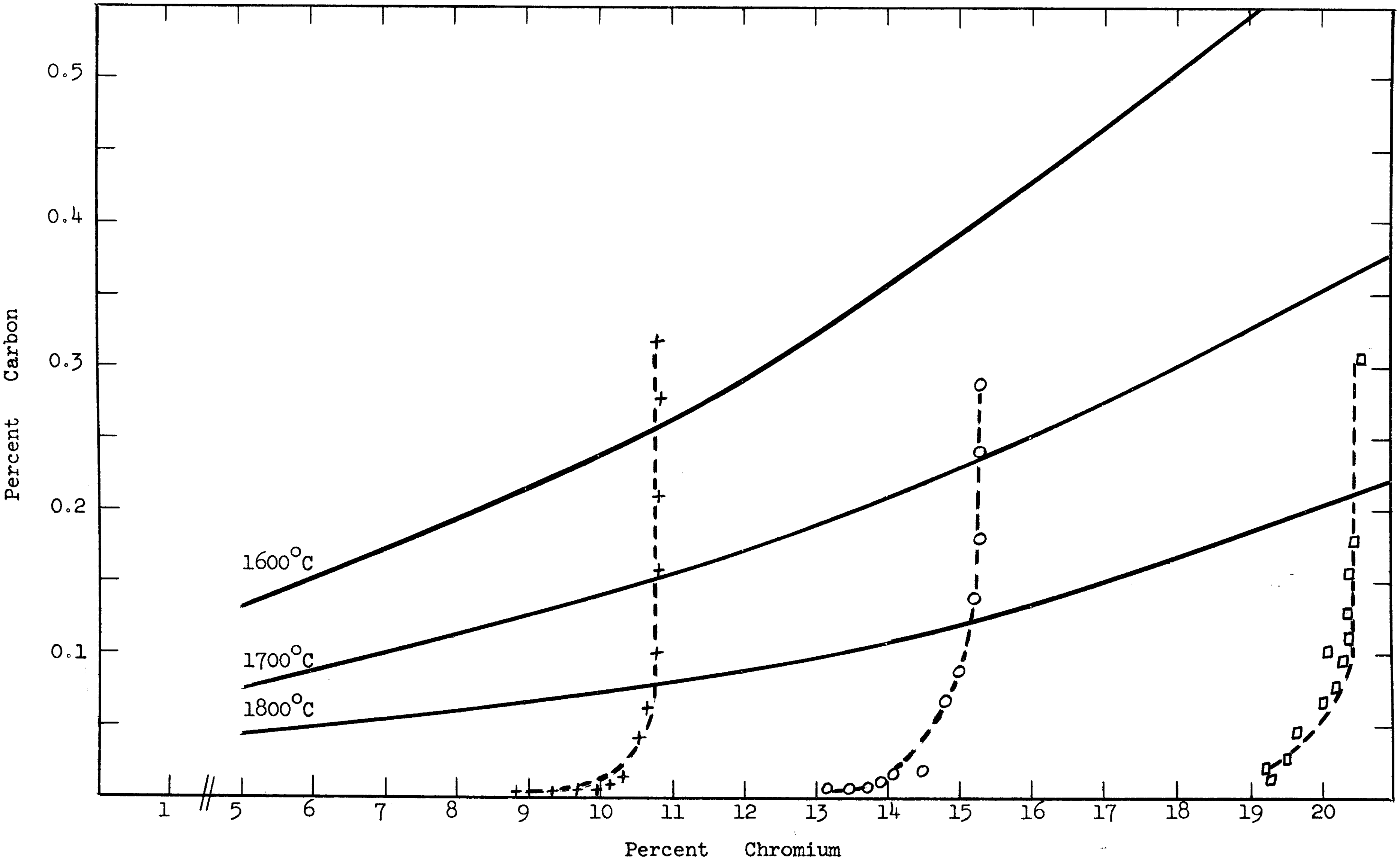

FIG. 12 CARBON - CHROMIUM RELATIONSHIPS, AIR BUBBLING

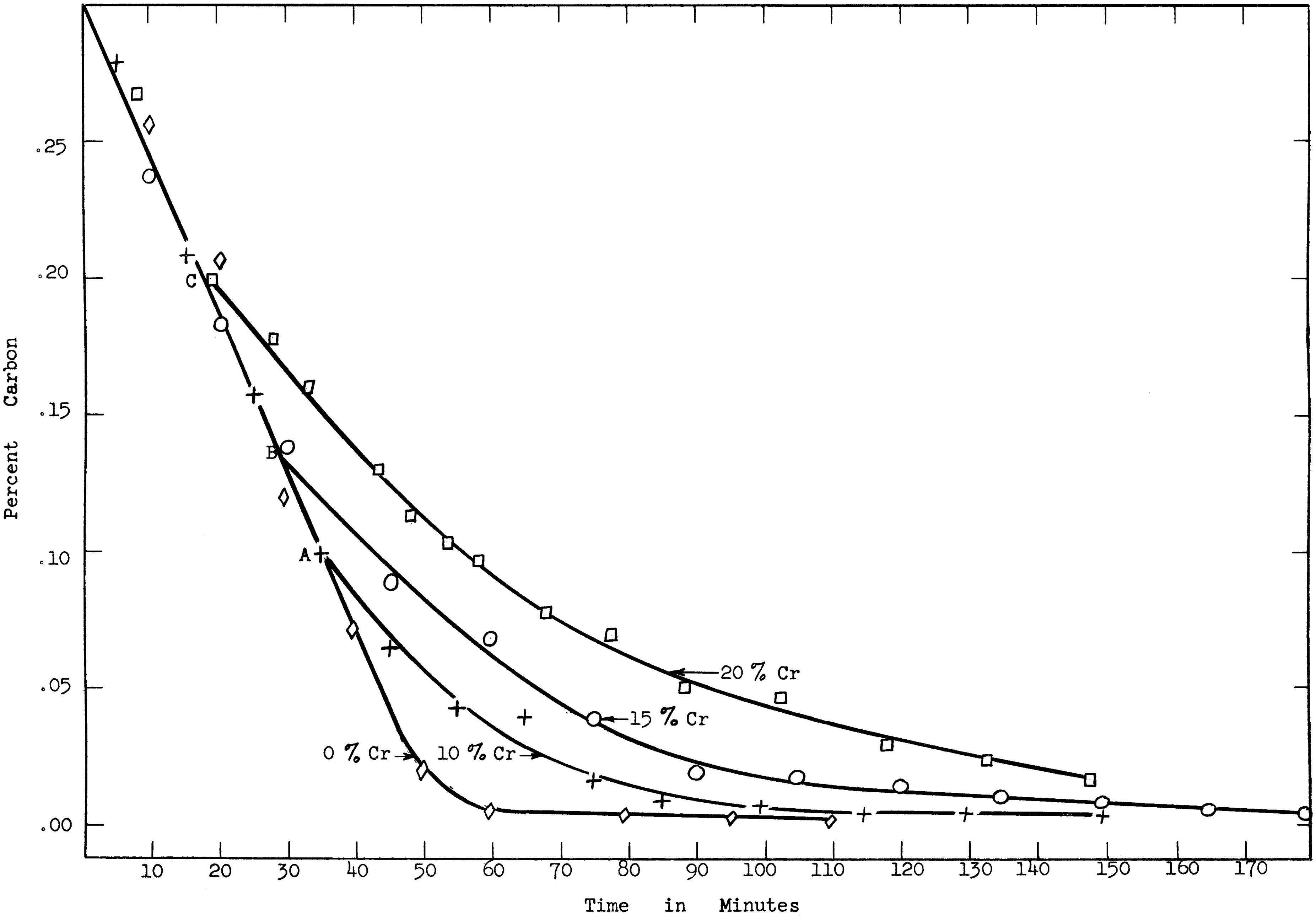

FIG. 13 CARBON OXIDATION RATES - AIR BUBBLING

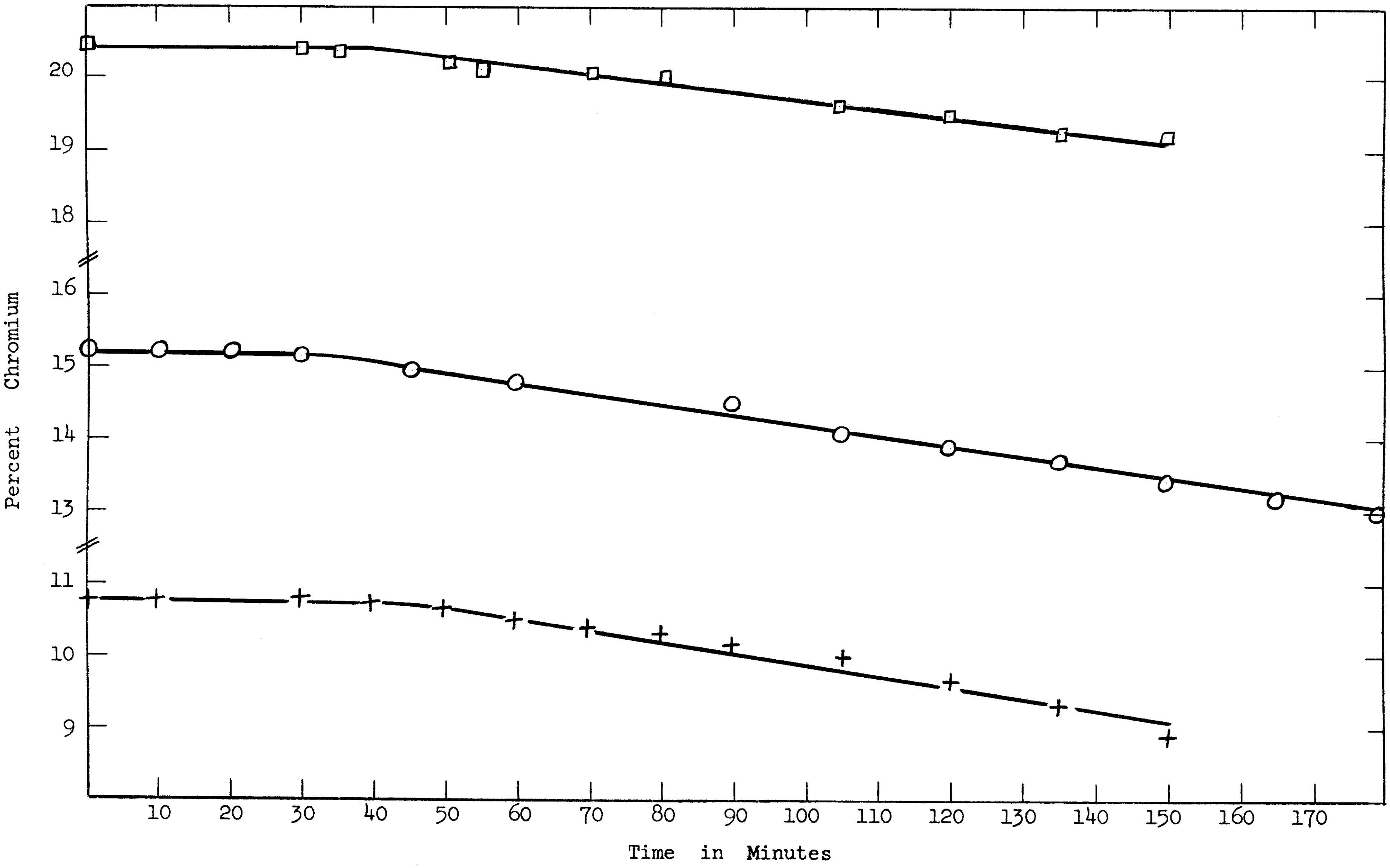

FIG. 14 CHROMIUM OXIDATION RATES - AIR BUBBLING

TABLE VII

Mass Balances - Total Oxygen Input vs. Carbon and Chromium Losses as CO and Cr_3O_4 During Air Bubbling

Percent	Oxygen Input	Carbon Loss	Chromium Loss		Moles O_2 As	
Chromium	in Moles	Gram Moles	Gram Moles	CO	Cr_3O_4	Total
10	0.42	0.31	0.45	0.15	0.30	0.45
15	0.50	0.29	0.52	0.14	0.35	0.49
20	0.42	0.30	0.34	0.15	0.23	0.38

suggests that control of the rate of carbon oxidation is by diffusion of carbon in the metal to the gas-metal interface.

Analysis of the rate of carbon loss beyond the point where the constant decarburization rate terminates is difficult, in view of the uncertainty regarding the oxide phase at the gas-metal interface. It was shown in the experimental air blowing runs, that the interfacial oxide cannot be considered to be Cr_3O_4, which is the equilibrium oxide for the chromium concentrations considered. Since it has been indicated by mass balances for the oxygen blowing runs that iron oxide is also present, a closer approach to the actual situation may be possible by assuming that the oxide phase is chromium spinel ($FeO.Cr_2O_3$) rather than Cr_3O_4. The equilibrium carbon activity with a partial pressure of carbon monoxide of 0.34 atmospheres may be calculated from the relationship:

$$FeO.Cr_2O_3(s) + 4\underline{C} = Fe(l) + 2\underline{Cr} + 4CO(g); \quad K_{1873^\circ K} = 1.29 \times 10^5.$$

For chromium concentrations of 10, 15, and 20 percent, the equilibrium carbon activities are 0.056, 0.064, and 0.072 respectively. These should represent the carbon activities at the gas-metal interface at the end of the constant rate of carbon oxidation. These carbon activities would be expected to be below the bulk carbon activities, which were found experimentally to be 0.059, 0.065, and 0.0705 respectively. Although these data suggest that the oxygen potential of the interfacial oxide is probably not quite that of $FeO.Cr_2O_3$, an approximate analysis is based on the assumption that the spinel is present.

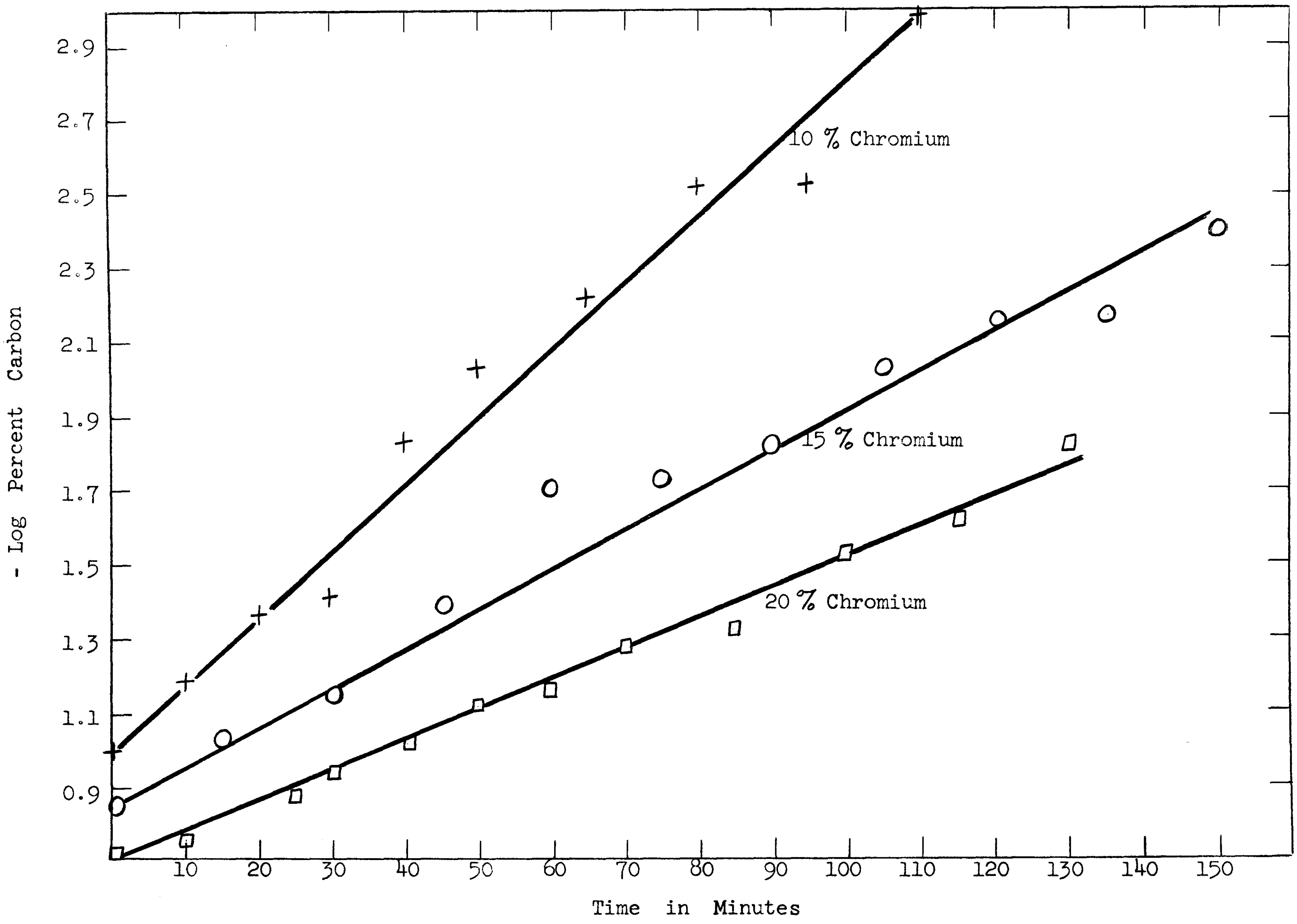

FIG. 15 LOGARITHM CARBON CONCENTRATION BELOW CONSTANT DECARBURIZATION RATE VS. TIME

With this assumption, the partial pressure of carbon monoxide at the reaction interface may be represented by the relationship:

$$(p^*_{CO})^4 = \frac{K \cdot \alpha_{FeO.Cr_2O_3} \cdot (f_C \cdot \% C^*)^4}{\alpha_{Fe} \cdot (\% Cr)^2} \qquad (8)$$

where $K = 1.29 \times 10^5$.

At 1600°C, and chromium concentrations of 10, 15, and 20 percent, the partial pressure of carbon monoxide is proportional to the interfacial carbon concentration. The further assumption is made, that the chromium concentration at the interface is approximately the same as the concentration in the bulk metal. This assumption seems justified on the basis of the slow rate of chromium loss during oxidation, the value of which was approximately 0.015 percent chromium per minute in the experimental runs. The rate of decarburization, at the point where the diffusion of carbon in the metal takes control, was 0.0056 percent carbon per minute. Considering the 10 percent chromium run, this occurred at a bulk carbon concentration of 0.10 percent, indicating that the carbon concentration gradient between the bulk metal and the gas-metal interface could be no greater than:

$$\% C' - \% C^* = 0.10$$

Assuming the diffusivity of chromium in iron to be similar to that of manganese, which was given as 10^{-4} square centimetres per second by King,[20] the mass transfer coefficients (D / δ) for carbon and chromium may be considered to be approximately equal. With equal interfacial area and melt volume, the experimental rate of chromium loss would be sustained by a maximum concentration gradient of :

$$\% \, Cr' - \% \, Cr^* = 0.25$$

At the concentrations of chromium under consideration, this maximum differential indicates little difference between the percentage chromium in the bulk metal and that at the gas-metal interface.

From equation (8), the proportionality between the partial pressure of carbon monoxide and the interfacial carbon concentration may be expressed for each level of chromium content:

$$(10 \% \, Cr) \qquad p^*_{CO} = 3.56 \, \% \, C^* \tag{9}$$

$$(15 \% \, Cr) \qquad p^*_{CO} = 2.32 \, \% \, C^* \tag{10}$$

$$(20 \% \, Cr) \qquad p^*_{CO} = 1.53 \, \% \, C^* \tag{11}$$

During the initial constant rate of decarburization, the oxygen supplied in the air reacts to form carbon monoxide. The partial pressure of carbon monoxide in the exit gas is, therefore, 0.34 atmospheres. This is also the partial pressure of carbon monoxide at the gas-metal interface. At the point where the rate of decarburization changes from the initial constant rate, the carbon concentration at the interface is assumed to be in equilibrium with $FeO.Cr_2O_3$, and with 0.34 atmospheres partial pressure of carbon monoxide. As the rate of arrival of carbon atoms to the gas-metal interface becomes insufficient to react with all of the oxygen, the oxidation of iron and chromium commences. The rate of formation of carbon monoxide therefore declines. It is assumed that the partial pressure of carbon monoxide in the gas bubbles emerging from the melt reaches equilibrium with the carbon concentration at the gas-metal interface.

This permits the rate of carbon loss from the bulk metal to be represented by the expression:

$$-\mathring{n}_C = \dot{n}_{gas} \cdot p_{CO} \qquad (12)$$

where $-\mathring{n}_C$ = rate of carbon loss in moles per minute.

$\dot{n}_{gas}$ = exit gas rate in moles per minute.

Taking the total pressure in the gaseous phase to be one atmosphere,

$$\mathring{n}_{gas} = \dot{n}_{N_2} + \mathring{n}_{CO} = \mathring{n}_{N_2} / (1 - p_{CO})$$

Substituting in equation (12), and expressing the rate of decarburization as percent carbon per minute, for the experimental melt weights of 1200 grams:

$$-d\,\%\,C/dt = \mathring{n}_{N_2} \cdot p_{CO} / (1 - p_{CO}) \qquad (13)$$

The partial pressure of carbon monoxide in the exit gas is changing during oxidation. This partial pressure, expressed in terms of the interfacial carbon concentration, as shown in equations (9), (10), and (11), is substituted in equation (13). Subsequent integration provides the following relationships:

$$(10\,\%\,\mathrm{Cr}) \quad \log\left(\frac{\%\,C_i^*}{\%\,C_f^*}\right) - 1.55\,(\%\,C_i^* - \%\,C_f^*) = 1.55\,\dot{n}_{N_2} \cdot t \qquad (14)$$

$$(15\,\%\,\mathrm{Cr}) \quad \log\left(\frac{\%\,C_i^*}{\%\,C_f^*}\right) - 1.01\,(\%\,C_i^* - \%\,C_f^*) = 1.01\,\dot{n}_{N_2} \cdot t \qquad (15)$$

$$(20\,\%\,\mathrm{Cr}) \quad \log\left(\frac{\%\,C_i^*}{\%\,C_f^*}\right) - 0.67\,(\%\,C_i^* - \%\,C_f^*) = 0.67\,\dot{n}_{N_2} \cdot t \qquad (16)$$

where t = time in minutes.

$\% C_i^*$ = initial interfacial carbon concentration.

$\% C_f^*$ = final interfacial carbon concentration.

With an air bubbling rate of 300 millitres per minute, $\dot{n}_{N_2}$ is equal to 0.0106 moles per minute.

Figure 16 presents the curves obtained by the solution of equations (14), (15), and (16), representing the change in interfacial carbon concentration with time, beyond the stage of constant decarburization rate, for chromium contents of 10, 15, and 20 percent. The points plotted for comparison are the bulk carbon analyses of the melts during air bubbling. In comparing the experimental bulk carbon concentrations with the predicted interfacial carbon concentrations, it will be noted that at the 10 and 15 percent chromium contents, the carbon concentration differential ($\% C' - \% C^*$) is very small. For the 20 percent chromium content, the carbon concentration differential is of larger magnitude. The diffusion gradient between the bulk carbon and the interfacial carbon may be considered to be a carbon activity gradient. For a similar carbon activity gradient, the effect of the higher chromium content is to increase the carbon concentration gradient, due to the effect of dissolved chromium on the activity coefficient of carbon.

The above analysis, although based on rather broad assumptions, provides a means of reasonable prediction of the rate of carbon oxidation beyond the point of departure from the initial constant decarburization rate.

The results of the experimental air bubbling runs show that the carbon concentration in the bulk metal, at the point of departure from the initial

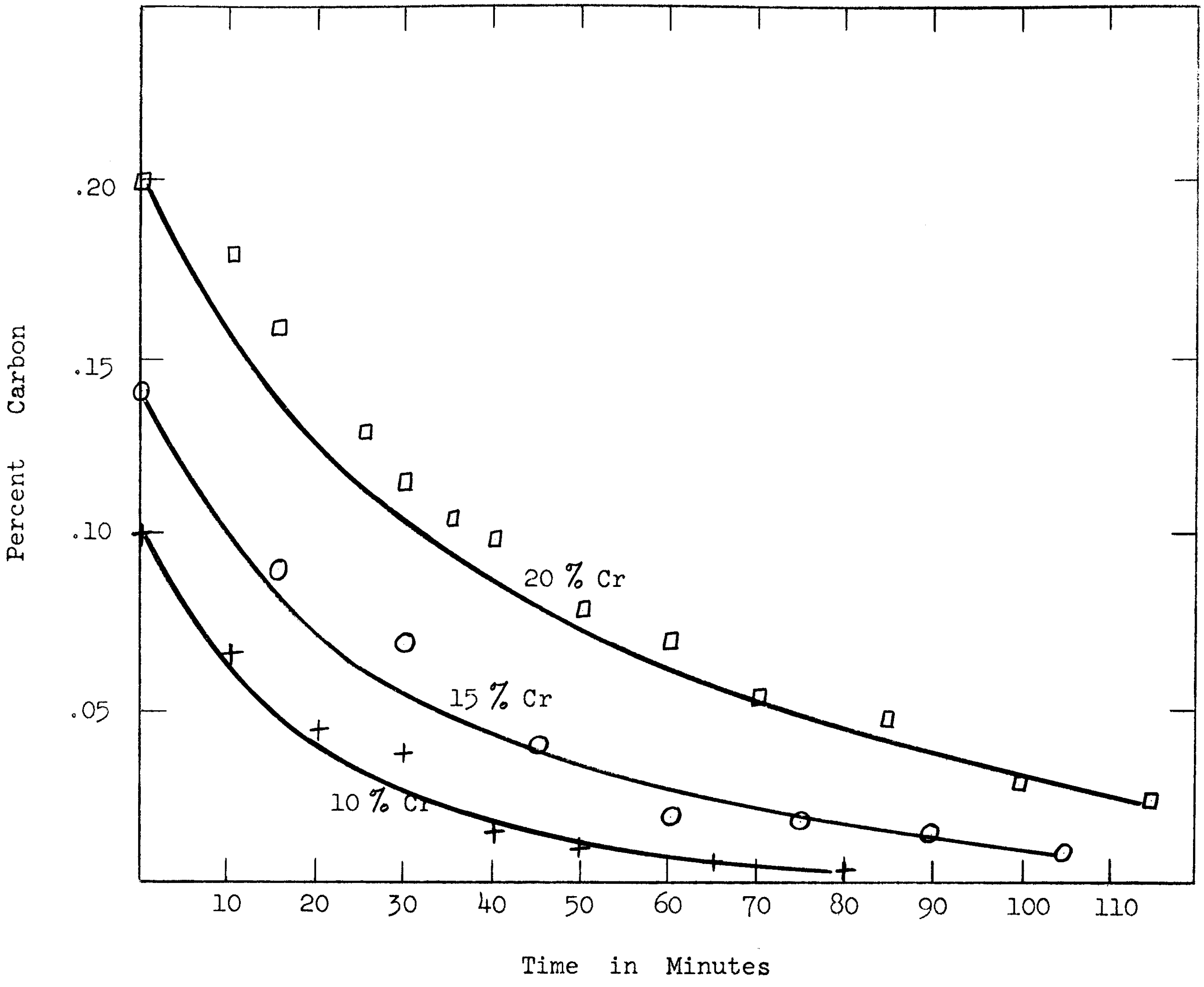

FIG. 16 CALCULATED INTERFACIAL CARBON CONTENT BELOW END OF LINEAR CARBON DROP VS. TIME; AIR BUBBLING - 300 ML. PER MINUTE

constant rate of carbon loss, was approximately equal to that calculated for the interfacial carbon concentration, assuming equilibrium with $FeO.Cr_2O_3$.

In the above analysis of the rate of change of the interfacial carbon concentration, it was assumed that the partial pressure of carbon monoxide in the exit gas reached equilibrium with the carbon concentration at the gas-metal interface. The rate of carbon loss from the bulk metal was determined experimentally, and shown in Figure 13. From the experimental results, the mean partial pressure of carbon monoxide in the exit gas may be calculated for ten minute intervals beyond the end of the constant decarburization rate. For the 10 percent chromium concentration, equation (9) provides the estimated mean interfacial carbon concentration for the time interval. By comparing this value with the experimental mean bulk carbon concentration for the time interval, an estimate of the carbon concentration gradient between the bulk carbon and the interfacial carbon may be obtained. The results of this estimate, for three intervals of ten minutes for the 10 percent chromium concentration are shown in Table VIII.

By substituting the experimental values of the rate of carbon loss and the estimated carbon concentration differential for each time interval in the relationship:

$$-d\,\%\,C/dt = \frac{A \cdot D_C^{Fe-Cr}}{V \cdot \delta_C} (\%\,C' - \%\,C^*) \qquad (17),$$

an average value is obtained:

$$A \cdot D_C^{Fe-Cr} / V \cdot \delta_C = 6.3 \times 10^{-3} \text{ sec.}^{-1}$$

TABLE VIII

Estimate of Carbon Concentration Differential Between Bulk Metal and Gas-Metal Interface, Beyond the End of Constant Decarburization Rate.

Time Interval in Minutes	Carbon Loss in Percent	Calculated Mean p_{CO}	Calculated Mean % C^*	Experimental Mean % C'	% C' - % C^*
0 - 10	0.036	0.25	0.070	0.08	0.010
10 - 20	0.021	0.17	0.048	0.054	0.006
20 - 30	0.013	0.11	0.037	0.040	0.003

An estimate of the bulk carbon concentration at the end of the constant rate of decarburization may therefore be obtained:

$$\%C' = -1.59 \times 10^2 \, (d\,\%C/dt) + \%C^* \qquad (18),$$

where $d\,\%C/dt$ = initial constant rate of carbon loss in percent carbon per second.

Richardson [22] has discussed the growth of carbon monoxide bubbles rising through the melt during an open hearth boil. The growth of the bubbles is considered to be controlled by the transport of carbon and oxygen from the metal to the gas-metal interface. The mass-transfer coefficient (D/δ) is taken as nearly independent of bubble size, and is estimated to be 0.05 centimetres per second for either carbon or oxygen. This was shown to compare favourably with an estimate of the mass transfer coefficient based on experimental work concerning the transfer of carbon dioxide between rising gas bubbles and water.

Considering the experimental melt depth of three centimetres in this present work, the number of bubbles that could reasonably be expected to reside in the melt would be two or three, assuming a bubble diameter of approximately one centimetre. This would provide a gas-metal interfacial area of approximately 8 square centimetres. Using this estimated area, along with the experimental melt volume, the mass transfer coefficient may be calculated:

$$D_C^{Fe\text{-}Cr} / \delta_C = 0.135$$

This value provides a diffusion boundary layer thickness (δ_C) of approximately one-third of that involved in Richardson's estimate of the mass transfer coefficient involved in the open hearth boil.

An application of the analysis described above has been made to predict the carbon oxidation rate curve for a 10 percent chromium alloy, having an initial carbon concentration of 0.39 percent. Oxidation was conducted by bubbling air at a rate of 450 millitres per minute (S.T.P.).

1. Initial rate of carbon oxidation = $- 1.3 \times 10^{-4}$ percent carbon per second.

2. Estimated termination of the constant rate of carbon oxidation, based on equation (18), $\% C' = 0.12$.

3. The interfacial carbon concentration beyond the constant rate of decarburization is calculated from equation (14),

$$\log \left(\frac{\% C_i^*}{\% C_f^*} \right) - 1.55 \, (\% C_i^* - \% C_f^*) = 2.46 \times 10^{-2} \, t$$

where $\% C_i^* = 0.10$, and t = time in minutes.

Figure 17 illustrates the result of these calculations, indicating the predicted interfacial and bulk carbon concentration during oxidation. The bulk carbon concentration beyond the end of the constant rate of carbon oxidation is shown as a gradual approach to the calculated interfacial carbon percentage, with a gradually decreasing gradient. Carbon analyses of samples taken during the experimental run are plotted for comparison. As seen in the figure, good agreement was obtained, indicating that the analysis has provided a reasonable prediction of the carbon oxidation rate

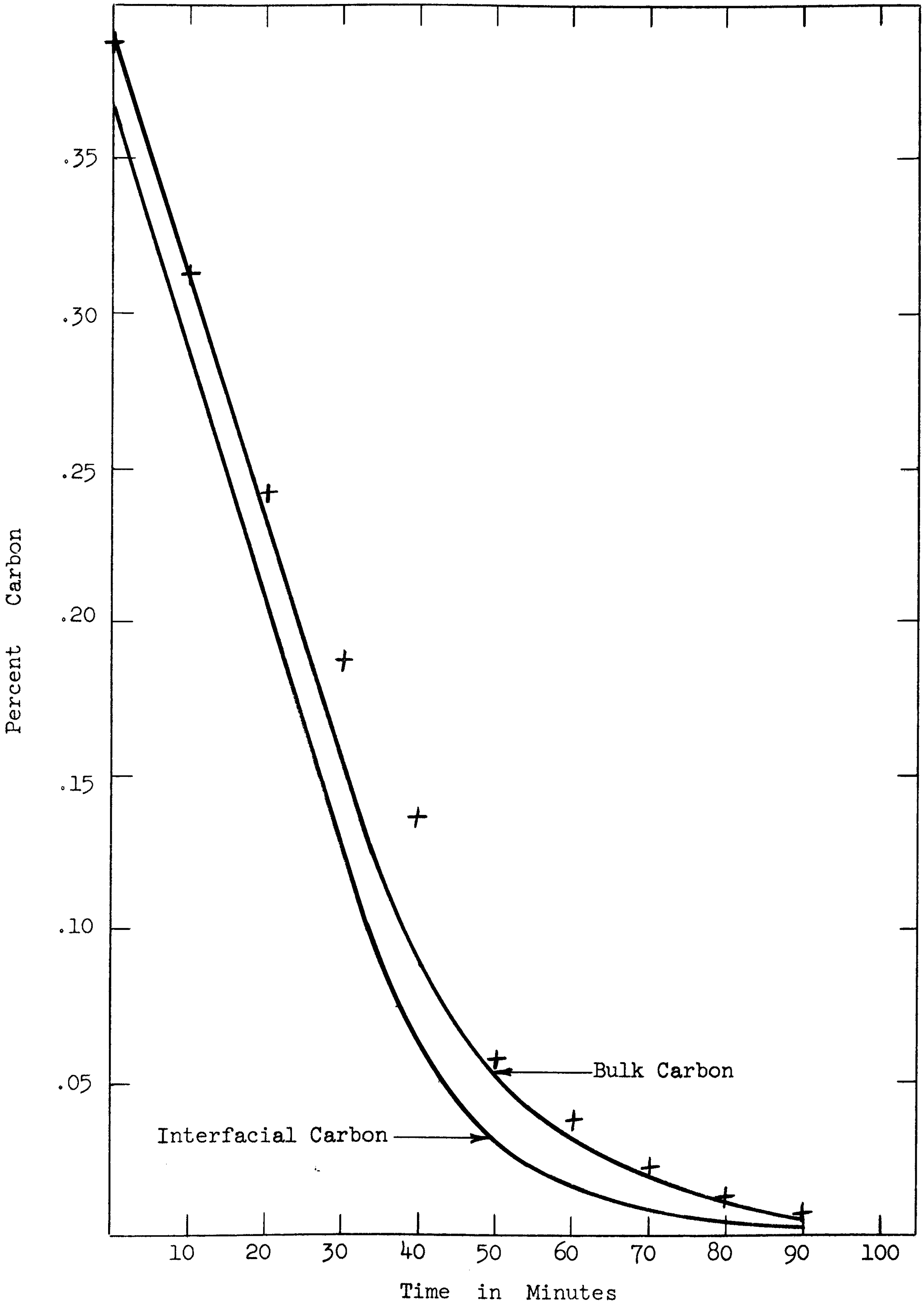

FIG. 17 PREDICTED INTERFACIAL AND BULK CARBON CONCENTRATION DURING AIR BUBBLING; AIR RATE - 450 ML. PER MINUTE

for the experimental conditions of oxidation. The experimental initial and final bulk carbon concentrations were 0.39 and 0.007 percent respectively. The initial and final chromium contents were 10.94 and 9.66 percent respectively.

Influence of Silicon on the Oxidation of Carbon and Chromium by Air Bubbling

The oxidation of carbon and chromium, dissolved in liquid iron, has been investigated in this work by the experimental bubbling of air through the melt. The influence of other oxidizable elements that are present in steelmaking baths was not considered. Since silicon is a strong deoxidizer, compared to chromium,[13] it was of interest to examine the influence of silicon on the initial decarburization rate and the loss of chromium, for the experimental conditions of oxidation.

An experimental run was conducted by bubbling air at a rate of 300 millitres per minute (S.T.P.) through an Fe-Cr-Si-C melt, with an initial composition of 0.5 percent silicon, 0.38 percent carbon, and 10.73 percent chromium. Figure 18 shows the rates of oxidation of carbon, silicon, and chromium that occurred. The presence of 0.5 percent silicon in solution did not alter the initial constant decarburization rate that was previously observed in melts containing no silicon. When the carbon oxidation rate deviated from constant, the oxidation of silicon began, while the chromium concentration remained unchanged. The start of chromium oxidation did not occur until the silicon concentration reached approximately 0.25 percent,

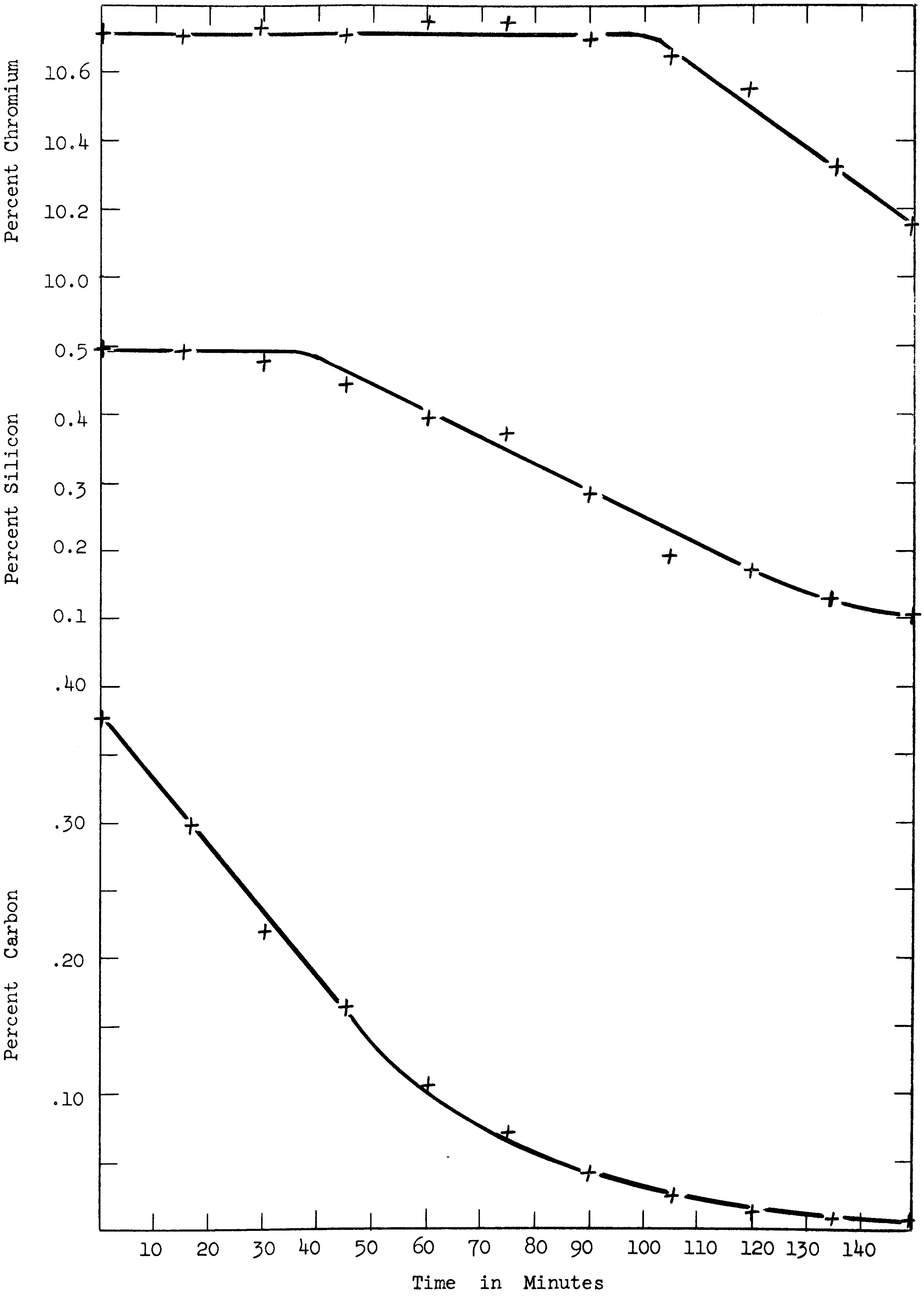

FIG. 18 INFLUENCE OF SILICON ON CARBON AND CHROMIUM OXIDATION - AIR BUBBLING

TABLE IX

Comparison of Carbon and Chromium Oxidation by Air Bubbling: (a) Fe-Cr-Si-C Melt; (b) Fe-Cr-C Melt.

Melt	Air Bubbling Rate Ml. per Min.(S.T.P.)	Oxidation Time in Minutes	Percent Carbon at End of Constant Decarb. Rate	Percent Carbon		Percent Chromium	
				Initial	Final	Initial	Final
Fe-Cr-Si-C	300	150	0.15	0.38	0.003	10.73	10.18
Fe-Cr-C	300	150	0.10	0.32	0.001	10.83	8.83

with a carbon content of approximately 0.02 percent.

The conclusion may be drawn that the overall decarburization was not altered by the presence of 0.5 percent silicon in solution. However, silicon oxidized in preference to chromium until the concentration of silicon reached 0.25 percent, following which the concurrent oxidation of chromium and silicon occurred, as carbon continued to drop at a much slower rate.

Table IX presents the results of oxidation of the Fe-Cr-Si-C melt, compared to an Fe-Cr-C melt that was also oxidized by air bubbling. In the case of the Fe-Cr-Si-C melt, the overall chromium loss was one-third of that which occurred in the Fe-Cr-C melt under the same conditions of oxidation. The effectiveness of the preferential silicon oxidation in delaying the oxidation of chromium is evident. The slightly higher carbon concentration at the end of the constant rate of decarburization, in the case of the silicon bearing melt, is probably due to the formation of SiO_2 at the gas-metal interface rather than iron and chromium oxides.

The Oxidation of Chromium in Iron - Chromium - Carbon Melts.

In the experimental runs conducted by oxygen blowing, it was evident that an initial oxidation period existed in which carbon oxidized preferentially, with no loss of chromium. Beyond this initial stage, when carbon loss deviated from a constant rate, the oxidation of chromium began. However, the rate of chromium loss was not dependent on the oxygen input rate. Although carbon oxidation to carbon monoxide, in the initial stage of oxidation, accounted for the entire oxygen input, the oxidation of carbon to carbon monoxide and chromium to Cr_3O_4 (the equilibrium oxide for the chromium concentration considered) did not account for the entire oxygen input during the second stage of oxidation. Further, it was found that chromium losses continued, along with carbon, during a holding period following the end of the oxygen blow, with argon passing through the furnace chamber.

It was shown that the oxidation of iron occurred with chromium during the second stage of oxidation. The continued oxidation of chromium following the end of the oxygen blow was due to an exchange reaction between the iron oxide formed and chromium in the metal.

It may be postulated that a hindrance to the oxidation of chromium exists, due to the difficulty involved in nucleating a solid oxide, the oxides of chromium being solid at the temperature involved. A hypothetical mechanism of chromium oxidation may be considered which involves the initial formation of iron oxide, with chromium oxide dissolving initially to the solubility limit. The solubility of Cr_2O_3 in FeO was investigated by Corning Research,[23] and the limit was shown to be from 5 to 10 percent at 1600°C. Beyond this solubility limit, it is expected that the spinel ($FeO.Cr_2O_3$) precipitates from solution. This hypothetical mechanism is supported by the visual observations of the metal surface during oxygen blowing. The first oxide observed was in the form of bright flashes which radiated from the gas-metal impingement area. This was followed by the formation of an oxide island, directly beneath the gas tube, which grew in size while dark areas formed within it. The island gradually enlarged over the entire surface of the metal, providing a crusty

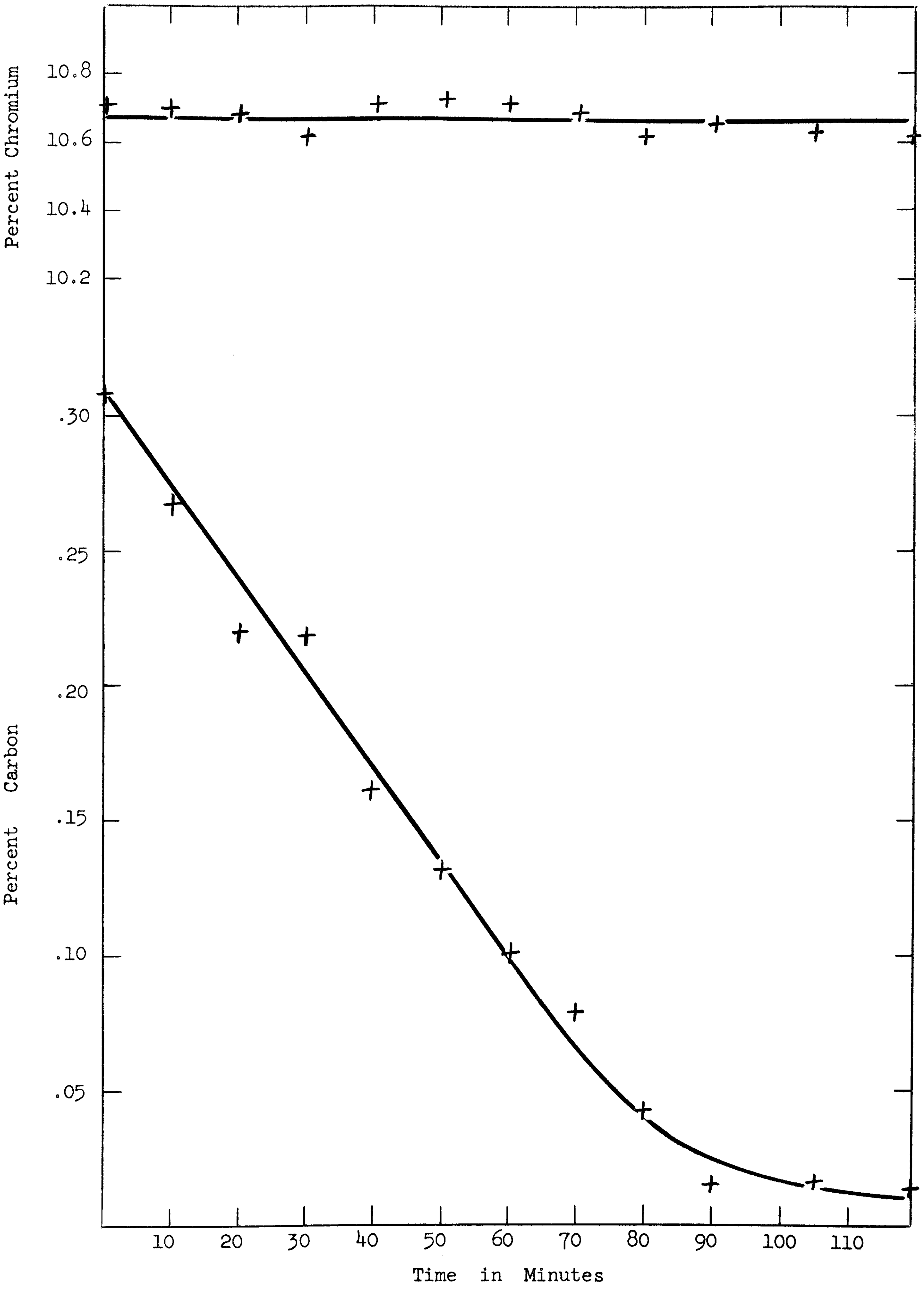

FIG. 19 OXIDATION OF CARBON AND CHROMIUM IN NICKEL BASE ALLOY - AIR BUBBLING

oxide covering.

As a consequence of the above hypothetical treatment of the mechanism of chromium oxidation, it would be presumed that in a situation where iron oxide was not present, the oxidation of chromium would be a more difficult process. To examine this possibility, a run was conducted in which nickel, having chromium and carbon in solution, was employed rather than iron. The melt was oxidized at 1600°C by bubbling air at a rate of 250 millitres per minute(S.T.P.).

Figure 19 presents the results of this run. During an oxidation period of 120 minutes, carbon oxidized readily to a low concentration, whereas the loss of chromium was almost negligible. In Table X, the results of the Ni-Cr-C run are compared to those from an Fe-Cr-C run in which oxidation was also by air bubbling. The very small change in chromium content for the Ni-Cr-C melt, in comparison with that which occurred in the Fe-Cr-C melt, indicates the difficulty involved in the direct nucleation of a solid chromium oxide and offers support to the mechanism of chromium oxidation suggested above.

In the oxidation of Fe-Cr-C melts by means of oxidizing gas, the oxide formed initially at the gas-metal interface during the second stage of oxidation (beyond the end of the constant decarburization rate) may be presumed to be iron oxide. This dissolves chromium oxide to the solubility limit, followed by the precipitation of chromium spinel. The oxidizing potential of the interfacial oxide was shown previously in this work to be nearly that of $FeO.Cr_2O_3$, for chromium concentrations from 10 to 20 percent.

TABLE X

Comparison of Carbon and Chromium Oxidation by Air Bubbling: (a) Dissolved in Ni; (b) Dissolved in Fe.

Melt	Air Bubbling Rate Ml. per Min. (S.T.P.)	Oxidation Time in Minutes	Total Air Volume - Ml.	Percent Carbon		Percent Chromium	
				Initial	Final	Initial	Final
Ni-Cr-C	250	120	30,000	0.308	0.014	10.72	10.62
Fe-Cr-C	300	100	30,000	0.32	0.009	10.83	10.10

VI. SUMMARY AND DISCUSSION OF EXPERIMENTAL RESULTS

In the preceding chapter, a discussion accompanied the presentation of the experimental results. In view of this, the present chapter will be concerned with a summary of the results, along with added discussion.

1. In the experimental oxidation of iron-chromium-carbon melts by the blowing of gaseous oxygen at relatively low rates on to the slag-free metal surface, it was shown that the oxidation of carbon occurred at the surface of the metal. During the initial stage of oxidation, a constant rate of decarburization existed which was dependent on the rate at which oxygen was supplied. Oxygen balances, calculated for the initial carbon oxidation, demonstrated that the formation of carbon dioxide was not involved, and that the reaction is described by the chemical equation:

$$\underline{C} + 1/2\ O_2\ (g) = CO\ (g).$$

The reaction between the dissolved carbon and oxygen gas consumed all of the oxygen supplied during the initial stage of oxidation, with no chromium loss. The constant decarburization rate ended at carbon concentrations which increased with increasing rate of oxygen input.

A hypothetical treatment of the situation at the end of the constant rate of carbon loss is based on the assumption that a thin film or boundary layer exists at the surface of the metal, through which the carbon diffuses from the bulk metal to the surface at which oxidation occurs. The end of the constant decarburization rate indicates the point at which the rate of carbon diffusion gains control of the rate of carbon oxidation. The rate that carbon diffuses through the boundary layer is dependent on the gradient between the carbon concentration in the bulk metal and the lower carbon concentration at the gas-metal interface. At the end of the constant rate of carbon drop, it may be presumed that the carbon gradient across the hypothetical boundary layer is not sufficient to transport the quantity of carbon atoms required by the oxygen available. At this point, the oxidation of iron and chromium begins.

Beyond the initial stage which was characterized by a constant decarburization rate, the rate of carbon loss declined rapidly. The final carbon content was, however, below that indicated by the equilibrium carbon-chromium relationships for carbon monoxide pressure of one atmosphere. In the initial experimental runs, with a furnace atmosphere consisting of the gaseous product of carbon oxidation, it may be assumed that the pressure of carbon monoxide existing at the gas-metal interface was one atmosphere. This suggested that the oxide formed at the gas-metal interface possessed a higher oxidizing potential than the equilibrium oxide (Cr_3O_4) for the chromium concentration involved.

During the second stage of oxidation, as the rate of decarburization decreased, the rate of chromium oxidation was independent of the rate of oxygen input. Despite increased oxygen blowing rates, the chromium oxidized at a rate showing no apparent change. Oxygen balances, taken over the total oxidation time, showed that the oxidation of carbon to carbon monoxide and chromium to Cr_3O_4 did not account for the total oxygen input.

2. Dilution of the furnace atmosphere by the entry of argon during oxygen blowing resulted in the carbon concentration dropping well below the equilibrium line. This demonstrated that the partial pressure of carbon monoxide at the gas-metal interface was lowered by the argon.

During a holding period following the oxygen blow, with continued passage of argon through the furnace chamber, the loss of both chromium and carbon continued. Oxygen balances, taken over the entire duration of the runs, demonstrated that the total oxygen input was accounted for by the formation of carbon monoxide and Cr_3O_4. During the second stage of oxidation, iron oxidized along with chromium. The FeO formed was in excess of that dissolved in the equilibrium oxide (Cr_3O_4). The solubility of FeO in Cr_3O_4 was reported to be approximately 10 percent by Hilty et al.[12] The result of iron oxidation was the subsequent reaction between carbon and chromium in the melt with excess FeO.

3. Investigation of the carbon and chromium concentration changes during a prolonged holding period under the oxide that was formed during the oxygen blow, demonstrated that carbon continued to oxidize to a very low level, with argon entering the furnace chamber. A straight line relationship was found between the logarithm of carbon concentration and the time of holding, which suggested that the diffusion of carbon in the metal to the gas-metal interface controlled the rate of carbon loss.

The oxidation of chromium continued during the first half of the holding period, followed by an increase in the chromium concentration in the metal during the remainder of the holding period. This increase in bulk chromium content was caused by reaction between the chromium oxide and the carbon in the metal. A similar carbon oxidation rate was observed by holding an iron-chromium-carbon melt under Cr_2O_3, with argon passing through the furnace chamber.

4. Investigation of the oxidation of carbon and chromium in liquid iron by means of air bubbling through the melt demonstrated that the oxide existing at the gas-metal interface during the stage where chromium oxidation occurs, is not the equilibrium oxide for the chromium concentration involved. By assuming this oxide to be $FeO.Cr_2O_3$, rather than the equilibrium oxide Cr_3O_4, a quantitative treatment of the experimental data provided a means of predicting the path of carbon oxidation for the experimental arrangement.

5. A hypothetical treatment of the mechanism of chromium oxidation was suggested, which involves the initial formation of iron oxide, followed by the precipitation of the chromium spinel from the FeO, as chromium oxide exceeds the solubility limit in FeO. This mechanism was supported by the experimental oxidation by air bubbling through a nickel-chromium-carbon melt. It was demonstrated that much more difficulty was involved in the oxidation of chromium in solution in nickel, compared to chromium oxidation when dissolved in iron.

The conditions involved in the experimental runs, conducted in this work, cannot be compared directly to the conditions existing in the electric arc furnace. The slag-free metal surface and the stirring effect of the induction coil are not involved in the production unit. However, possible causes may be inferred qualitatively, for the disagreement between the theoretical and the actual oxygen requirements in stainless steelmaking that was noted earlier in this work. The oxide formed at the oxygen-metal interface during the oxygen blow is not the equilibrium oxide of chromium, but one that has a greater oxidizing potential than the equilibrium oxide. Also, in the author's experience, the slag covering the metal becomes crusty and solid during the oxygen blow. This could permit the formation of carbon monoxide at the metal surface, by reaction between carbon in the metal and the solid oxide, with the partial pressure of carbon monoxide at the metal surface lowered by the effect of the furnace atmosphere. These two factors would permit the carbon concentration in the melt to fall below that indicated by the carbon-chromium relationships ($p_{CO} = 1$ atmosphere).

From the practical standpoint, the effective oxidation of carbon to very low concentration with relatively small chromium losses, which was experienced during air bubbling through the experimental melts, merits consideration. Although the time for carbon removal to a low concentration with air bubbling would certainly be increased over that required with oxygen blowing, the effect of the decreased loss of chromium in minimizing the slag reduction procedures must be considered as well. The rate of carbon oxidation, following the initial constant decarburization rate, is represented by the relationship:

$$\frac{-d\,\%\,C}{dt} = \frac{A \cdot D_C^{Fe-Cr}}{V \cdot \delta_C} \quad (\%\,C' - \%\,C^*).$$

Considering this relationship qualitatively, the rate of carbon loss is dependent on the gas-metal interfacial area (A), the effective boundary layer thickness (δ_C), and the interfacial carbon concentration ($\% C^*$). The interfacial area would depend on the rate of air input, the depth in the melt at which the air is entered, and the diameter of the gas input tube or tubes. A small effective diffusion boundary layer thickness would be assured by the agitation effect of the rising bubbles. A very low interfacial carbon concentration is attainable, as demonstrated experimentally.

The carbon concentration at the gas-metal interface declines according to a relationship having the form:

$$\log \left(\frac{\% C_i^*}{\% C_f^*} \right) - k\,(\% C_i^* - \% C_f^*) = k' \cdot t$$

In this relationship, $\% C_i^*$ and k depend on the chromium concentration and temperature of the metal. The constant k' is dependent on the chromium concentration, temperature, and the rate of air input.

Certainly these considerations require thorough investigation under production conditions in order to demonstrate their validity in a melting furnace operation. However, based on the evidence of the experimental runs conducted in this present work, the oxidation of carbon to very low concentration with relatively small losses of chromium is feasible.

VII. SUGGESTIONS FOR FURTHER WORK

In the course of the investigation of the parallel oxidation of carbon and chromium in liquid iron, the experimental procedure of air bubbling through the melt demonstrated the removal of carbon to very low concentration with a relatively small concurrent loss of chromium. The effective and highly preferential oxidation of carbon by this method merits consideration in practical application.

The experimental conditions which involved the stirring effect of the induction coil and the absence of a slag cover, do not permit comparison with steelmaking furnaces in the case of the blowing of oxidizing gases. However, the conditions existing during air bubbling would not be seriously influenced by the considerations just mentioned. It is concluded, therefore, that investigation of the oxidation of carbon in iron containing chromium, by means of air bubbling under production furnace conditions is warranted.

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APPENDIX

TABULATION OF EXPERIMENTAL RESULTS

I. Oxygen Blowing, Furnace Atmosphere Carbon Monoxide.

Run No. 23 - Oxygen rate - 120 ml. per min.; Charge - 1500 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.41	9.84
2	5	0.39	9.85
3	15	0.30	9.76
4	20	0.26	9.75
5	30	0.20	9.70
6	40	0.18	9.50

Run No. 24 - Oxygen rate - 200 ml. per min.; Charge - 1500 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.65	9.74
2	10	0.52	9.65
3	20	0.39	9.68
4	30	0.27	9.75
5	40	0.21	9.48
6	50	0.189	9.38
7	60	0.184	9.12

Run No. 25 - Oxygen rate - 250 ml. per min.; Charge - 1500 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.60	10.11
2	5	0.53	10.13
3	10	0.44	10.01
4	15	0.35	10.03
5	20	0.29	9.98
6	25	0.25	9.80
7	35	0.21	9.71

II. Oxygen Blowing, Furnace Atmosphere Diluted by Argon.

Run No. 30 - Oxygen rate - 100 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.32	9.98
2	10	0.24	9.98
3	20	0.15	9.98
4	30	0.09	9.92
5	40	0.07	9.76
6	50	0.04	9.61
	Time Held		
7	15	0.03	9.62
8	30	0.02	9.57

Run No. 34 - Oxygen rate - 150 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.46	10.80
2	10	0.32	10.74
3	20	0.21	10.76
4	30	0.14	10.61
5	40	0.14	10.39
6	50	0.12	10.18
7	60	0.10	10.06
	Time Held		
8	15	0.077	9.83
9	30	0.057	9.68
10	45	0.052	9.57

Run No. 35 - Oxygen rate - 225 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.46	10.57
2	5	0.38	10.73
3	10	0.28	10.62
4	15	0.21	10.56
5	20	0.16	10.63
6	25	0.14	10.52
7	30	0.12	10.40
	Time Held		
8	15	0.076	10.16
9	30	0.059	10.08
10	45	0.035	10.04
11	60	0.028	---

Run No. 37 - Oxygen rate - 100 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.38	14.70
2	10	0.31	14.60
3	20	0.24	14.60
4	30	0.20	14.65
5	40	0.16	14.41
6	50	0.15	14.24
7	60	0.14	14.18
	Time Held		
8	15	0.11	14.14
9	30	0.077	14.11
10	45	0.070	14.02
11	60	0.051	13.93

III. Reduction of Chromium Oxide by Carbon. Furnace Atmosphere Diluted by Argon.

Run No. 32 - Oxygen rate - 120 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.41	9.72
2	50	0.15	9.22
	Time Held		
3	15	0.10	9.07
4	30	0.043	9.02
5	45	0.022	9.08
6	60	0.010	9.18

Run No. 40 - Added 30 grams Cr_2O_3 to melt surface. Furnace atmosphere diluted by argon. Charge - 1200 grams.

Sample No.	Holding Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.20	10.73
2	10	0.13	10.73
3	20	0.065	10.97
4	30	0.037	10.92
5	40	0.032	11.04
6	50	0.017	11.09
7	60	0.011	11.06
8	70	0.005	11.07
9	80	0.005	11.06

IV. Oxidation by Air Blowing.

Run No. 65 - Air rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.35	20.86
2	10	0.26	20.67
3	20	0.21	20.65
4	30	0.19	20.67
5	40	0.16	20.59
6	50	0.13	20.62
7	60	0.11	20.51
8	70	0.09	20.39
9	80	0.07	20.41
10	90	0.065	20.37

Run No. 66 - Air rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Time of Blow in Minutes	Percent Carbon	Percent Chromium
1	0	0.36	10.85
2	10	0.29	10.81
3	20	0.23	10.76
4	30	0.19	10.75
5	40	0.11	10.71
6	50	0.08	10.72
7	60	0.052	10.62
8	70	0.047	10.60
9	80	0.030	10.51
10	90	0.024	10.48

V. Oxidation by Air Bubbling.

Run No. 61 - Air rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.32	10.83
2	10	0.28	10.87
3	20	0.21	---
4	30	0.16	10.83
5	40	0.10	10.81
6	50	0.064	10.68
7	60	0.043	10.53
8	70	0.042	10.47
9	80	0.014	10.37
10	90	0.009	10.21
11	105	0.006	10.00
12	120	0.003	9.68
13	135	0.003	9.36
14	150	0.001	8.83

Run No. 58 - Air Rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.291	15.27
2	10	0.237	15.27
3	20	0.183	15.23
4	30	0.142	15.17
5	45	0.090	14.99
6	60	0.069	14.83
7	75	0.039	---
8	90	0.018	14.50
9	105	0.018	14.07
10	120	0.015	13.98
11	135	0.009	13.77
12	150	0.007	13.49
13	165	0.008	13.18
14	180	0.004	13.02

Run No. 59 - Air rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.308	20.58
2	10	0.270	---
3	20	0.200	---
4	30	0.180	20.48
5	35	0.161	20.41
6	45	0.131	20.40
7	50	0.114	20.27
8	55	0.104	20.12
9	60	0.098	20.35
10	70	0.078	20.24
11	80	0.070	20.19
12	90	0.052	---
13	105	0.049	19.72
14	120	0.029	19.57
15	135	0.024	19.28
16	150	0.014	19.37

Run No. 60 - Iron-Carbon Melt. Air rate - 300 ml. per min.; Charge - 1200 g.

Sample No.	Bubbling Time in Minutes	Percent Carbon
1	0	0.39
2	10	0.33
3	20	0.26
4	30	0.21
5	40	0.12
6	50	0.075
7	60	0.020
8	70	0.004
9	80	---
10	90	0.003
11	105	0.002
12	120	0.001

VI. Oxidation by Air Bubbling, Increased Rate.

Run No. 69 - Air rate - 450 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.391	10.94
2	10	0.316	10.88
3	20	0.246	10.82
4	30	0.191	10.74
5	40	0.141	10.62
6	50	0.059	10.43
7	60	0.041	10.39
8	70	0.024	10.17
9	80	0.013	10.05
10	90	0.007	9.89
11	100	0.007	9.66

VII. Oxidation by Air Bubbling, Iron-Silicon-Chromium-Carbon Melt.

Run No. 47 - Air rate - 300 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Silicon	Percent Chromium
1	0	0.38	0.50	10.73
2	15	0.30	0.50	10.73
3	30	0.22	0.48	10.76
4	45	0.17	0.45	10.72
5	60	0.11	0.40	10.78
6	75	0.072	0.38	10.78
7	90	0.041	0.29	10.71
8	105	0.023	0.20	10.67
9	120	0.012	0.18	10.58
10	135	0.0062	0.14	10.35
11	150	0.0034	0.11	10.18

VIII. Oxidation by Air Bubbling, Nickel-Chromium-Carbon Melt.

Run No. 63 - Air rate - 250 ml. per min.; Charge - 1200 grams.

Sample No.	Bubbling Time in Minutes	Percent Carbon	Percent Chromium
1	0	0.308	10.72
2	10	0.268	10.72
3	20	0.220	10.69
4	30	0.220	10.61
5	40	0.163	10.73
6	50	0.136	10.74
7	60	0.103	10.71
8	70	0.081	10.70
9	80	0.043	10.63
10	90	0.016	10.67
11	105	0.017	10.64
12	120	0.014	10.62

BIOGRAPHICAL NOTE

The author was born on October 16, 1925, in Port Colborne, Ontario, Canada. He graduated from Queen's University, Kingston, Ontario, Canada, in 1947, with the Baccalaureate Degree of Bachelor of Science in Metallurgical Engineering, and received the Gold Medal, awarded for academic honours.

During the period from 1947 to 1961, the author was associated with Atlas Steels Limited, Welland, Ontario. His responsibilities during part of these years involved metallurgical quality control of production practices in the melting and processing of specialty steels. In this area, he held positions such as Metallurgist and Metallurgical Engineer in charge of Mill Metallurgy. During the balance of the author's industrial experience, he entered production management, having responsibility for the Continuous Casting operations and subsequently holding the position of Melting Department Superintendent.

In 1961, the author entered the Graduate School at the Massachusetts Institute of Technology, as a candidate for the Degree of Doctor of Philosophy.

The author is a member of the Association of Professional Engineers, Province of Ontario; the American Institute of Mining, Metallurgical, and Petroleum Engineers; and the American Society for Metals.

Publications in which the author has participated in writing, include:

1. " Aircraft Quality Steels," Electric Furnace Steel Proceedings, A. I. M. E., 15, 142, (1957).
2. " Continuous Casting at Atlas Steels,' Journal of Metals, A. I. M. E., 9, 1050, (1957).