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THE INFLUENCE OF PRESSURE ON THE CARBON-OXYGEN REACTION IN 0.21 PCT. CARBON-IRON MELTS SUBJECTED TO REDUCED PRESSURES OF CARBON MONOXIDE

by
Arlan Edward Rathke

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Stephen K. Sarby
Professor in charge

Head of the Department

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ABSTRACT

The pressure dependency of the reaction

$$\underline{C} + \underline{O} = CO(g)$$

in molten iron was investigated by the induction melting of 15 lb charges containing initially 0.21 wt. pct. carbon and 0.0162 wt. pct. oxygen under various reduced pressures of carbon monoxide. The charges were contained in high purity alumina crucibles. Each charge was melted, equilibrated for 30 min. and sampled at 600 mm Hg. of CO before the pressure was reduced to that desired for investigation. Pressures investigated were 200, 100, 50, 20, 10, 5, 2, 0.5, and 0.05 mm Hg.

The results of this investigation showed that no significant removal of oxygen occurred at pressures less than 100 mm Hg. of CO. The constant oxygen values obtained at the lower treatment pressures were thought to be the result of a balance between the oxygen removed from the melt as carbon monoxide and the oxygen fed into the melt by means of a melt-crucible reaction. Attempts to determine the extent of the melt-crucible reaction were made by analyzing the melts for dissolved aluminum content. This approach yielded no meaningful information. Therefore, several types of melt-crucible reactions which could account for the observed experimental results were discussed. The carbon contents for all melts were found to decrease with treatment time. The amount of decrease was found to be independent of the experimental conditions prevailing for each individual melt. It was postulated that the carbon consumed in excess of that required for the observed oxygen removal represented a measure of the overall reactivity of the refractory material in contact with the melt.

The experimental results of this investigation were compared with values calculated from thermodynamic relationships. It was found that the results obtained at 600 mm Hg. of CO were in excellent agreement with values calculated from the theoretical considerations of the carbon-oxygen reaction. Below chamber pressures of 600 mm Hg., the experimental values showed considerable deviation from theoretical values. The amount of deviation did not appear to be pressure dependent. These results were interpreted as an indication that the reaction is governed by thermodynamic considerations above 600 mm Hg. and by kinetic considerations at the lower pressures.

INTRODUCTION

The reaction of oxygen with carbon dissolved in molten iron is one of the most important if not the most important reaction in steelmaking technology. This reaction must be considered in the refining of pig iron to steel and in the solidification process. The theoretical and operating aspects of the carbon-oxygen reaction have been the subject of many extensive investigations which have been carried out over the past twenty-five years. While the results of these investigations have led to a better understanding of the various steelmaking processes and ingot solidification, the problems encountered with the utilization of the carbon-oxygen reaction in steelmaking are far from being completely solved.

One problem of extreme importance is associated with the use of the carbon-oxygen reaction in the refining of pig iron to steel. As the carbon content of the melt is decreased by the reaction of oxygen with the dissolved carbon, the solubility of oxygen in the molten iron increases. Thus, while some impurity elements are being removed by the process of oxidation, the process itself is adding another impurity, i.e. dissolved oxygen. This dissolved oxygen may be a problem in the solidification process and very definitely influences the quality of finished steel products. Therefore, molten steel is generally treated with additions of strong oxide forming elements such as silicon or aluminum to remove or control the oxygen. Unfortunately, the product of the reaction between dissolved oxygen and the deoxidizer is generally a solid at steelmaking temperatures. While some of the reaction product will float out of the steel prior to solidification, much of the material will be entrapped in the finished steel as nonmetallic inclusions. These inclusions plus those which are formed during solidification are detrimental to the quality and mechanical properties of finished steel products.

The ideal deoxidizer would be one which would produce a gaseous reaction product. From this standpoint carbon could be used as a deoxidizer since the product of the carbon-oxygen reaction is gaseous. Unfortunately, at atmospheric pressure the carbon-oxygen reaction is not as complete nor as efficient as the reactions involving metallic deoxidizers. Thermodynamics indicate that the carbon-oxygen reaction is pressure dependent. Therefore, if steel is subjected to pressures less than atmospheric, carbon can be utilized as an effective deoxidizer.

Large tonnage vacuum treatment of liquid steel was introduced by the steel industry as a means of preventing hydrogen flaking in flake sensitive grades without the use of long-time hydrogen diffusion heat treatments. This particular application of vacuum treatment, commonly called vacuum degassing, has proven to be highly successful and has been put into use throughout the steel industry. Some deoxidation is also accomplished during treatment for hydrogen; however, the flake sensitive grades of steel are alloy steels which are generally deoxidized prior to vacuum treatment. Thus, this type of steel does not represent a good test for the potential of vacuum carbon deoxidation. Experimental work on steel grades more conducive to deoxidation by carbon has been undertaken; however, the experimental results are generally not in good agreement with those predicted from theoretical considerations.

LITERATURE REVIEW

A considerable amount of literature has been published concerning the utilization of vacuum degassing for the removal of dissolved hydrogen. An excellent review paper on industrial practices and results has been prepared by Mund[1]. It is interesting to note that various industrial users have developed their own designs for the physical equipment and that the final hydrogen contents and the treatment pressures vary from installation to installation. The end result, however, has been that regardless of the molten metal configuration which is exposed to pressures ranging from 0.3 to 8 mm Hg., the processes have been capable of eliminating the hydrogen flaking problem.

The differences in pressure, final hydrogen contents, and yet the elimination of flaking are at first puzzling as the removal of hydrogen from molten steel is governed by Sievert's law. This law states that the solubility of diatomic gases, which dissolve in the monoatomic state, is proportional to the square root of the partial pressure of that particular gas over the melt surface. In other words, as the partial pressure is lowered, the dissolved gas content will also be lowered. In this respect, the experimentally obtained final hydrogen contents are in good agreement with those predicted from theory.

A possible explanation for the difference in equipment and operating procedures and yet the elimination of the flake problem has recently been published by Hornak[2] who, in describing the results of a United States Steel research program on hydrogen removal, states:

> "As expected the flaking sensitivity of the steels studied varied with the composition, with the rate of cooling and with

the hydrogen content of the steel. This study clearly demonstrated that if flaking is to be avoided, the vacuum facility must be capable of decreasing the hydrogen content of the most flake sensitive steel produced to a level that will prevent flaking under the steel handling practices being used. Thus the final hydrogen requirement of one melt shop can differ from that of others which explains why some melt shops are satisfied with higher hydrogen levels after vacuum degassing than others."

A recent article[3] concerned with the latest developments in the evolution of vacuum degassing in the steel industry presents a good review of the current work on vacuum carbon deoxidation. In most cases, equipment and pressures identical to those utilized for hydrogen removal are being used for deoxidation. Notable exceptions are two units, designed expressly for deoxidation, which operate at pressures ranging from 50 to 100 microns. The pressures for these units were apparently chosen by the theoretical consideration that the lower the pressure, the more efficient the carbon-oxygen reaction becomes.

An indication of the effectiveness of the various bath configurations and treatment pressures is shown in Figure 1, which was taken from Hrnak's article[2]. While the exact bath configuration (i.e., physical equipment) is not stated, the use of the pressures and reference 3 are sufficient to indicate that most types of vacuum treatment are represented. Another point of caution in the use of Figure 1 is that the exact steel grade and steelmaking practices are not acknowledged. Regardless of these factors, Figure 1 shows that the oxygen content after vacuum treatment is not a function of the treatment pressure in the range of 0.1 to 8 mm Hg. A comparison of these experimental values with values calculated from theory shows that the experimental values lie considerably above the theoretical values calculated for the highest operating pressure. In fact, the experimental oxygen values differ from the theoretical ones by a factor of approximately 20.

The thermodynamic aspects of the carbon-oxygen reaction in molten iron-carbon-oxygen alloys were first extensively investigated by Marshall and Chipman[4]. The results of this work include a value for the thermodynamic equilibrium constant of the reaction

$$\underline{C} + \underline{O} = CO(g) \tag{1}$$

and the pressure dependency of this reaction for pressures ranging from 1 to 20 atmospheres. Marshall and Chipman's results have been confirmed by other investigators. The most recent work on this subject is that of Ban-ya and Matoba[5]. From these equilibrium studies have come the predictions for equilibrium carbon and oxygen contents in molten iron baths subjected to pressures less than one atmosphere.

Thomas and Moreau[6] in 1946 experimentally studied the above predictions by the vacuum induction remelting of small steel samples containing known amounts of carbon and oxygen. The remelting was carried out in magnesia crucibles at various pressures of nitrogen for short periods of time. The pressures considered in this study were 760, 260, 60, 26, 6, and 0.01 mm Hg. The results of this study showed that the reaction of carbon and oxygen was indeed pressure dependent below one atmosphere. However, the values obtained did not agree with those predicted from Chipman's work. Another interesting feature of this early work was that a considerable amount of carbon was lost during a run. These large carbon drops were attributed to a melt-crucible reaction which proceeds simultaneously with the deoxidation reaction.

The widespread use of vacuum induction melting brought about a number of investigations into the production of pure iron by carbon deoxidation. The results of these studies indicated that there exists a minimum oxygen content below which it is impossible to remove oxygen to a greater degree. Comparison of these types of data with values calculated from Chipman's work led Samarin[7] to conclude that there was little reason to deoxidize in vacuum at pressures below 3 mm Hg. Samarin further justifies his statement by stating that the ferrostatic head of the melt is an inherent limitation in the approach to equilibrium conditions by a melt. Moore[8] proposed that under vacuum the minimum oxygen content is not determined by equilibrium considerations for the carbon-oxygen reaction, but rather by a balance between two competing reactions, i.e., deoxidation of the melt and contamination of the melt by a reaction with the crucible.

Machlin[9] has developed a model which considers vacuum refining to be controlled by kinetic rather than thermodynamic considerations. A confirmation of the theory has been published by Turillon and Machlin[10] who conducted experiments on the carbon deoxidation of pure iron by vacuum induction melting. This work clearly showed that the deoxidation of pure iron is limited by the reaction of the melt with the crucible.

The influence of a crucible reaction upon the final oxygen content of various iron-carbon alloys has been reported by Bennett, Protheroe, and Ward[11]. This particular study, conducted at 2 microns pressure, involved the melting of a series of iron-carbon-oxygen alloys ranging from 0.10 to 0.85 pct. carbon in magnesia crucibles in order to study the influence of carbon content, time of vacuum treatment, and agitation (produced by either rocking the crucible or by argon-lancing) upon the efficiency of deoxidation. An important result of this study, aside from the crucible reaction, was that although agitation assists in obtaining lower oxygen values, the values still differed considerably from those determined from theoretical considerations. The influence of the crucible reaction on the results of this work could not be determined quantitatively as the important reaction product, Mg, is gaseous under conditions of the experiment.

Studies concerned with the determination of the minimum oxygen content attainable in pure iron and iron-carbon-alloy heats melted in various crucible materials have been conducted by a number of investigators. Darling[12] presents a review of some of this work which illustrates some of the problems encountered in the study of melt-crucible interaction. In one case, ball-bearing steel was remelted in beryllia, magnesia, or alumina crucibles. The oxygen content was practically eliminated in beryllia and alumina crucibles, but reached a constant level of 0.01 pct. in magnesia. These data are in direct contradiction with that of Bosworth[13] and Winkler[14] who showed that the lowest oxygen contents can be obtained in magnesia crucibles. Winkler's study is particularly interesting as ball-bearing steel was the subject of the investigation. The suitability of a crucible refractory appears to depend upon the major refractory constituent, the amount and type of impurity oxides, and the composition of the melt. A systematic study of these variables has yet to be conducted.

Meadowcroft and Elliott[15] have presented a theoretical review of the type and extent of the various reactions which must be considered in the vacuum treating of metals. This paper's major value to experimental work in the field is that it points out that the determination of the exact mechanism by which certain final results are obtained may prove to be an impossible task. Some of these reactions will be considered in the discussion of the experimental results of this investigation. Another theoretical paper by Meadowcroft[16] considers the process of vacuum carbon deoxidation from a standpoint of carbon monoxide bubble nucleation and growth. A major conclusion of this work is that the use of extremely low pressures for deoxidation is not required as the external pressure is not the controlling factor. Meadowcroft suggests that, in general, pressures less than 7.6 mm Hg should not be required for efficient deoxidation. A comparison of Meadowcroft's predicted pressure with the industrially obtained values shown in Figure 1 shows again the lack of agreement between experimental and theoretical values.

EXPERIMENTAL DETAILS

A review of the literature has shown that although a considerable amount of work has been done in vacuum carbon deoxidation from both industrial and laboratory standpoints, a clear understanding of the many variables involved in the process has not been obtained to date. It appears that a systematic investigation of the variables would be beneficial. Therefore, it was decided to limit the present investigation to an extensive study of only one major variable.

One of the most basic problems encountered in vacuum carbon deoxidation is the pressure dependency of the carbon-oxygen reaction under reduced pressures. It has been theoretically suggested that reaction kinetics and not thermodynamics is the governing factor. The kinetic theory is very ably supported by experimental determinations conducted at very low vacuums. It would be interesting, from an industrial standpoint, to know at what point the transition from thermodynamic to kinetic factors occurs.

It has been suggested that the observed deoxidation results represent a steady-state condition between the carbon-oxygen reaction and the reaction of the melt with the crucible material. Therefore, any study conducted on vacuum carbon deoxidation should include a means of evaluating the extent of the melt-crucible reaction.

The objectives of this investigation were established to be as follows:

(1) To study the pressure dependency of the carbon-oxygen reaction in molten carbon-iron-oxygen melts subjected to pressures of less than one atmosphere, and

(2) To determine the extent of the melt-crucible reaction by the use of a suitable refractory. Major considerations on this point include the selection of a high purity material and an oxide material which, upon reaction with the melt, will produce a metallic product capable of being retained by the melt.

The size of the experimental equipment to be utilized for the above program constitutes a major decision. Most laboratory studies concerned with iron and steelmaking parameters have been carried out on melts ranging in size from 20 to 200 grams. Generally, each melt yields one experimental data point. The suitability of these small systems for work on the carbon-oxygen reaction at low pressures is questionable on the basis of work reported in the literature. Turillon and Machlin[10] have shown that the rate of carbon loss in a 100 lb. vacuum furnace is greater than that in a 300 lb. furnace. It appears that a possible or partial explanation for the very large carbon drops obtained by Thomas and Moreau[6] is melt size (250 grams). Similar carbon drops can be found in the work of Turner[17] who utilized melts of approximately 200 grams. Bennett and coworkers[11], utilizing 25 lb. melts and magnesite (MgO) crucibles, did not report carbon drops as extensive as those of Thomas and Moreau or Turner.

Although the use of a large melt size generally means that a number of samples will be taken from the same melt, the total volume of such systems is such that the removal of a number of suitably sized samples will not significantly influence the refractory-melt contact area to volume ratio for melt. A melt size of fifteen pounds was chosen for this study.

Equipment

The vacuum system utilized in this work was a modified Stokes Model 437-520 Precision Casting Vacuum System. As purchased, the system consists of a double-walled chamber, a vacuum pumping section, induction heating equipment, and control consoles for power and vacuum.

The vacuum chamber is constructed with stainless steel interior surfaces surrounded by a carbon steel water jacket. The interior dimensions of the chamber are 30 in. high by 22 in. wide by 15 in. deep. Access to the chamber is made through a full opening, aluminum alloy door which is sealed with an "O" ring flange. An externally controlled, circular turntable covers most of the bottom of the chamber. In addition to an 8 in. access port, the chamber has a 3 in. diameter shuttered sight glass, a long bore sight tube, a bridge breaker assembly, and various-sized, tapped and capped ports which can be utilized for the installation of various accessories.

The vacuum pumping system has a common 6 in. manifold which supports two 4 in. Stokes Ring-Jet Booster pumps. These pumps are, in turn, connected to a common exit which leads to an 80 cfm Stokes Microvac mechanical vacuum pump. An isolation valve is provided in the line between the booster and mechanical pumps.

The induction heating equipment is of Inductotherm design which operates on a frequency of 3000 cycles per second with a maximum power input to the coil of 30 kilowatts. Power is carried to the furnace coil by flexible, water-cooled leads which connect to a tilting coaxial power feed assembly. The connection between the furnace coil and the feed assembly is made by means of nuts which are tightened against flanged tubes. Vacuum tightness is insured by means of "O" rings.

The vacuum system is controlled from a completely self-contained console. The controls for the vacuum system are so wired that the entire vacuum system is automatically controlled by an "On-Off" switch. An automatic timer is included in the circuit so that the booster pump oil can be cooled before the vacuum chamber and pump area are exposed to the atmosphere. The console contains two electric vacuum gauges; namely, one with a pressure scale of 0 to 1000 microns and the other from 0 to 20 mm Hg. The sensing heads for these gauges are located in the manifold above the first booster pump and in the exhaust line between the booster pumps and the mechanical pump, respectively.

The system described above was found to be unsatisfactory for studies on vacuum deoxidation in the as-purchased condition. Therefore, extensive modifications were made to all parts of the system. These modifications were not undertaken in any particular sequence, but rather were made as operation of the system revealed the need.

A Stokes immersion thermocouple assembly was installed in the appropriate location on the vacuum chamber. The original installation was such that the angle of entry of the thermocouple to the bath was quite shallow and prevented sufficient penetration of the bath. The assembly was modified so that the thermocouple entry was perpendicular to the bath surface. Other modifications made to the chamber included: (1) the installation of a new turntable to raise the molds to a more suitable pouring height and to aid in positioning the molds, and (2) a connection in the back wall of the chamber to permit pressure measurements by means of thermocouple, McLeod, or mercury manometer vacuum gauges. In addition, all "O" ring seals were replaced and all joints were cleaned and coated with glyptal.

The connection between the power feed assembly and the furnace coil was changed as the original connection was so badly pitted that arcing occurred in the joint when approximately one-half of the rated power was applied. Further application of power was prohibited until the vacuum had been broken and the joint had been retightened. The new joint is of a male-female, force fit design. Alignment and vacuum tightness is accomplished by means of adjustable split-brass rings containing "O" ring seals. This arrangement is capable of operating at the maximum rated power.

The remainder of the modifications to the basic system were concerned with the vacuum system. In the first place, the automatic nature of the vacuum controls made it impossible to operate the mechanical pump independent of the booster pumps. The controls were rewired so that the mechanical pump operation was not dependent upon the booster pumps. The other shortcoming of the original system was that there existed no means of isolating the chamber from the pumps. This feature prevented a rapid determination of the chamber leak-rate from a low vacuum level and the operation of the vacuum melting equipment under a static pressure. Therefore, a 6 in. manually operated gate valve was installed in the manifold between the chamber and the opening for the first booster pump.

The modified vacuum system is shown in Figures 2 through 4. The system is capable of attaining an ultimate vacuum level of 1 to 2 microns in the chamber. This vacuum level was found to deteriorate at the rate of approximately 0.06 microns per min. (cold leak rate) under suitable conditions. It is felt that these vacuum conditions, i.e., level and rate of deterioration, were sufficient to eliminate several sources of extraneous oxygen from consideration in the experimental program.

Materials

The 15 lb. furnace charges consisted of electrolytic iron and enough carbon-saturated iron to produce an initial carbon content of 0.21 pct. In order to insure compact and reproducible charges, the electrolytic iron chips were melted in a 500 lb. vacuum induction furnace and cast into ingots. The resulting ingots were forged into 3 1/2 in. diameter rounds. The surface of the rounds was removed by machining to prevent the introduction of any oxide material. The resulting rounds were cut into appropriately sized lengths for charging into the crucible. Before charging, the melting stock was washed in carbon tetrachloride to remove any cutting fluid which may have adhered to the surfaces.

The carbon-saturated iron was prepared by vacuum induction melting electrolytic iron chips with graphite. The material was cast as a thin sheet which permitted the material to be broken into appropriately sized chunks. The chemical composition for the electrolytic iron melting stock and the carbon-saturated iron are given in Table I.

All experimental runs were made using 17 lb. capacity Norton Alundum 213, heavy wall crucibles. A typical chemical analysis for these crucibles is presented in Table I. Originally, the crucible backing material was Norton E163 bubbled alumina insulating grain and the top seal and pouring spout was constructed with Norton RA1162, high alumina refractory. The use of both items was discontinued early in the experimental program, as they were thought to be possible sources of oxygen. The majority of the runs were made using coarse Lava LaMag 32E as the crucible backing material and fine Lava LaMag 32E bonded by a 50-50 solution of waterglass and water as the top seal and pouring spout material. A typical chemical analysis for LaMag 32E may be found in Table I.

The vacuum chamber geometry is such that a limitation exists on the number of molds that can be accommodated for pouring; therefore, with the 15 lb. melt size, the crucible could not be emptied at the completion of a run and approximately 10 lb. was left to solidify in the crucible. This practice necessitated the use of a new alumina crucible for each experimental run. Prior to use, each crucible and the accompanying top seal and pouring spout was fired at approximately 2000°F under a vacuum of 1-2 microns until a hot-leak-up rate of less than 10 microns per min. was obtained. Under normal conditions, the hot-leak-up rate for the various crucible setups averaged 2 microns per min. The firing process was carried out by induction heating of a graphite susceptor which had been placed within the alumina crucible.

Linde High Purity Dry (99.995%) argon and Matheson C. P. Grade (99.5% minimum) carbon monoxide were utilized in the program.

The immersion thermocouple was protected with quartz tubes obtained from the Thermal American Fused Quartz Company. A new protection tube was used for each experimental run.

Operational Techniques

A number of different operating procedures were tried during the program in order to determine the technique best suited for the objectives of the program. The sampling, temperature measurement, and analytical phases of all procedures were, however, similar.

Sampling

The molten bath was sampled as a function of time by pouring approximately 1 lb. of material into a 1 in. diameter by 5 in. long cavity in a machined, split, 3 in. square steel block mold. The surfaces of the cavity were coated with a colloidal graphite suspension to prevent sticking of the sample pin. It was found that a small amount of pure aluminum was required in each mold to insure the production of a sound casting. Samples for chemical analysis of each sample pin were obtained in the following manner:

> The bottom 1/4 in. of the pin was removed and discarded. A full diameter, 1/4 in. disc was then cut and submitted for oxygen analysis. Next two full diameter, 1/2 in. discs were cut and were utilized for carbon and aluminum analyses, respectively. Finally, another full diameter, 1/4 in. disc was obtained for oxygen analysis. The balance of the sample pin was identified and stored in the event that further analytical specimens be required.

Temperature Measurement

The temperature for each experimental run was monitored by a calibrated, platinum-platinum-10 pct. rhodium immersion thermocouple enclosed in silica sheaths and by a Leeds and Northrup optical pyrometer sighted through a long bore sight tube located above the bath surface. The output of the thermocouple was fed directly into a Leeds and Northrup Speedomax H recorder having a temperature scale ranging from

2000 to 3200°F. Temperature control for each run was established in the following manner:

> After the charge was completely molten, the power input to the coil was varied until appropriate and constant optical pyrometer readings were obtained. The immersion thermocouple was then inserted and a temperature correction was obtained for the optical pyrometer reading. In general, this correction factor was 400°F. The true temperature of the bath at any instant was, therefore, the optical temperature reading plus approximately 400°F. The optical pyrometer was utilized throughout a run for temperature control while the immersion thermocouple was utilized only as a "check". On the average, three immersion readings were obtained during the course of a run lasting one hour.

Analyses

All oxygen contents were determined using a Bendix-Balzar Exhalograph which is located at the Homer Research Laboratories of the Bethlehem Steel Corporation. The accuracy of each determination is reported to be ±0.0003 wt. pct. oxygen. At least four oxygen determinations were run on each sample pin. Two place carbon contents for each sample were determined by a standard combustion method having an accuracy of ±0.005 wt. pct. carbon. The silicon content for each sample was determined spectrographically. Both wet chemical and spectrographic aluminum determinations were performed.

Procedures

The experimental runs may be divided into five groups. Each grouping is based upon the utilization of slightly different melting practices. These groupings are briefly described below:

Group I: Included in this group are runs 1 through 3. The first run was an attempt to melt down under a pressure of 1-2 microns. An extremely violent carbon boil was observed and the run was terminated. Runs 2 and 3 were melted down under a pressure of 380 mm Hg. of argon. As soon as the bath was molten, the pressure was reduced toward the final pressure of 1-2 microns. Troubles developed during both runs and the final pressure was never attained. The crucibles from this group of runs showed signs of alteration which were believed to be caused by oxygen contamination.

Group II: Since the crucibles from the Group I runs showed signs of alteration which were thought to be caused by oxygen contamination from the backing material, the bubbled alumina was replaced with LaMag 32E. Runs 4 and 5 utilized this backing material. The final pressure objective was also changed to 20 mm Hg. This pressure is based upon the calculations of Schaffer[18] who shows by means of thermodynamic calculations that the melt-crucible reaction for alumina refractories and 0.40 pct. carbon-iron becomes critical at partial pressures of carbon monoxide of 16.90 mm Hg. The charges were melted down under 380 mm Hg. of argon. Temperature control and the pouring of one sample pin were accomplished before the pressure was reduced to 20 mm Hg. Additional samples were taken at the 20 mm Hg. pressure level.

<u>Group III</u>: Although no difficulties were encountered with the Group II runs, a question arose in regard to "the time at pressure" variable. Therefore, it was decided to hold the pressure constant throughout the course of a run. Run 6 was made under 20 mm Hg. of argon, while runs 7 through 9 utilized a furnace atmosphere of 20 mm Hg. of carbon monoxide. Severe bridging upon meltdown was observed for all runs in this group. It was thought that the bridging problem was caused by the vigorous carbon boil which starts as soon as melting begins. The boil expels metal droplets from the liquid pool which then solidify on the cooler, upper portion of the crucible, and as a consequence weld part of the solid charge in place. The strong bath reaction can be explained by the high oxygen content of the starting materials (162 ppm) and the low melting pressure.

<u>Group IV</u>: Because of the bridging problems encountered with Group III runs, it was decided to investigate the carbon deoxidation reaction at reduced pressures of carbon monoxide by melting and equilibrating the charges at a relatively high carbon monoxide pressure and then reducing chamber pressure to that desired for investigation. Temperature control and the pouring of a sample were to be accomplished at the higher pressure level. Since the objective of this work is to determine the pressure dependency of the carbon oxygen reaction under reduced pressures, it would be desirable to set the equilibration pressure at one atmosphere where comparisons with previous published data could be readily made. However, the vacuum chamber previously described is not capable of being operated at or above 1 atmosphere pressure. Rather than undertake the required modifications, it was decided to use 600 mm Hg. as the

equilibration pressure. The procedure for this group of runs was as follows. Charges were melted down and equilibrated for 30 minutes after the bath was completely molten under a chamber pressure of 600 mm Hg. of carbon monoxide. Temperature control was established during the 30 minute time period. A sample was obtained at the end of the equilibration period. The pressure in the system was then reduced to that chosen for the particular run. Sampling and temperature control were practiced at the new pressure level. Runs 10 through 25 were made according to the Group IV procedure. Pressures investigated were 200, 100, 50, 20, 10, 5, 2, 0.5 and 0.05 mm Hg.

Group V: One of the objectives of this program was to study the extent of the melt-crucible reaction by using alumina crucibles, which upon decomposition should feed aluminum to the melt. Early chemical analyses of the pin samples failed to show any substantial aluminum pickup.

Parlee and coworkers[19] have reported that when carbon monoxide was introduced after charges had been melted in alumina under vacuum, a crust of alumina formed on the bath surface. This information was utilized to determine if aluminum was present in melts of this study. The procedure followed for run 26 consisted of a 30 minute equilibration of the molten charge at 600 mm Hg. of carbon monoxide, a rapid reduction in the pressure to 20 mm Hg., and finally, an increase in the pressure to 200 mm Hg.

Detailed Procedure for Group IV Runs

Since the majority of the experimental runs were made using the Group IV operating procedure, a detailed account of the various operations performed in preparation for a run and during a run of this group is presented below.

After the furnace coil assembly and the molds from the previous run have been removed from the chamber, the interior chamber surfaces were first subjected to a blast of compressed air to remove some soot and the beads of metal that had been ejected from the bath during reduced pressure treatment. The chamber surfaces and the door area were washed with carbon tetrachloride to remove the last traces of soot. The thermocouple sheath was changed and any repairs required on the thermocouple were made at this point. The new furnace coil assembly with a new alumina crucible, top seal, and pouring spout already in place was installed and the joint tested for water tightness.

The graphite susceptor for baking was placed within the crucible and the door "O" ring was cleaned and coated with Dow Corning Silicone High Vacuum grease. The door was then closed and the vacuum pumps turned on. Pumping was continued until a vacuum level of 1-2 microns was reached. The cold leak rate was then determined by closing the manifold valve and noting the increase in pressure as a function of time. If a satisfactory leak rate (2-5 microns per min.) was obtained, the manifold valve was opened and power was progressively applied to the furnace coil until a temperature reading of approximately 1650°F could be obtained with the optical pyrometer sighted on the graphite susceptor. Baking of the crucible assembly was continued until a vacuum level of 1-2 microns was reached. At this point, the hot leak rate was determined by closing the manifold valve and noting the pressure increase as a function of time. If the hot leak rate was 2 microns per min. or less, the power was shut off and the crucible assembly was allowed to cool under vacuum. If the desired hot leak rate was not attained, the manifold valve was reopened and baking was continued until the desired value was reached. Generally, eight hours at approximately 2000°F (optical reading plus correction factor) were sufficient to obtain the desired hot leak rate.

After the crucible assembly had cooled to room temperature, the chamber was evacuated to a level of 1-2 microns and the cold leak rate was determined. At this point, the cold leak was found to be approximately 0.1 microns per min. or less. The manifold valve was then closed, the booster pumps placed on cooling cycle, and the chamber was opened by admitting argon to 1 atmosphere pressure. The graphite susceptor was removed and the molds were positioned on the turntable. The slugs of electrolytic iron and the carbon-saturated iron chips were then placed in the crucible and the chamber was sealed. The chamber was evacuated to a level of 1-2 microns and allowed to outgas until the previous cold leak rate value was again obtained.

The manifold valve was closed, booster pump placed on cooling cycle, and the chamber pressure was increased to 380 mm Hg. by the introduction of argon. After the booster pumps had cooled, the manifold valve was opened and the chamber again evacuated to a level of 1-2 microns. The manifold valve was then closed, booster pumps placed on cooling cycle, and the chamber pressure was increased to 600 mm Hg. by the introduction of carbon monoxide. Power was then applied to the coil.

After the charge was molten, the pressure was adjusted to 600 mm Hg. by rapidly opening and closing the manifold valve. The power input to the coil was varied to obtain a constant optical temperature reading.

An immersion thermocouple reading was then taken. After 30 minutes had elapsed from the time the charge became molten, the furnace was tilted to pour a sample. The chamber pressure was then reduced to the new desired pressure level by opening and closing the manifold valve. The decrease in pressure was followed using either the thermocouple gauges or the manometer. After the new pressure level had been established, the temperature was adjusted using a combination of optical and immersion readings. Additional samples were taken at time intervals of 45, 55, and 65 min. from the time the charge became molten. At the end of the allotted time for each run, the power was turned off, and the bath was allowed to solidify under the chamber pressure for the particular run. It was observed that bath surfaces became frozen approximately 2 minutes after the power had been turned off.

It should be noted that aside from induction stirring the only bath agitation was that obtained by the tilting of the furnace for sampling and that resulting from the change in chamber pressure.

RESULTS

The operational details of all experimental runs are given in Table II. Included is information concerned with the temperature, treatment time, operating pressure, gas species, and sampling procedure. This information together with the general comments previously given affords a good resume of the procedure utilized for each run.

It will be noted that all runs made using the Group I procedure were of an exploratory nature and thus yielded no meaningful information. The two runs produced using the Group II procedure were made without encountering any serious difficulties. In run 6 made using the Group III procedure with argon as the chamber atmosphere, the turntable mechanism became jammed which brought about an early termination of the run. Bridging was encountered in runs 7, 8, and 9, which were made according to the Group III procedure using carbon monoxide as the chamber atmosphere.

Runs 10 through 25 were made according to the Group IV or equilibration procedure. Runs 10, 13, and 16 yielded no meaningful information because of pouring difficulties, vacuum pump failure, and power failure, respectively. Duplicate runs were made at second pressure levels of 200 mm Hg. (runs 12 and 21), 0.5 mm Hg. (runs 15 and 23), and 0.05 mm Hg. (runs 24 and 25).

Chemical analyses for all successful runs are presented in Table III. The oxygen values reported are the average of the determinations performed on both sample positions. Where a difference exists between sampling positions, two average values are shown. In general, the sample pins were found to be homogeneous with respect to carbon and oxygen content. As previously stated, the addition of a small amount of aluminum to the sample molds was required to produce a sound casting. The weight of this aluminum addition and the pin weight were determined so that the percent aluminum deliberately added could be accurately known. These values are also listed in Table III. The aluminum concentrations reported in Table III were determined by spectrographic and wet chemistry techniques. The particular technique utilized for a given experimental run is denoted in the table. The silicon content of each sample is also given in Table III. Sample letters A through D indicate samples which were poured into the pin molds, while sample letter E indicates samples which were taken from the material that was solidified in the crucible at the end of each run.

Diagrams showing the variation of carbon and oxygen concentrations as a function of treatment time are presented in Figures 5 through 17.

DISCUSSION

A major concern in this program was the capability of the previously described experimental equipment to provide reproducible results. Runs 4 and 5, produced using the Group II procedure, were made under identical conditions in so far as melt composition, temperature, and partial pressure of argon are concerned. The results of these runs, which are presented in Table III and Figure 5, show that the carbon and oxygen contents are quite reproducible between runs.

Further evidence for the reproducibility of the system can be found by consideration of runs 6 through 9 made using the Group III operating procedure. The data for these runs can be readily compared with the aid of Figure 6.

Several interesting items are apparent from a consideration of the data of the Group II and III runs. It appears that the oxygen contents of these melts rapidly approach a constant value of approximately 25 ppm. This value appears to be independent of the operational technique utilized. The carbon content of these runs did not exhibit a constant behavior pattern such as that shown by the oxygen contents. The carbon content decreased in each run with the rate of decrease and the final carbon content being some function of each particular type of run.

Runs 10 through 25 have been used to establish the pressure dependency of the carbon deoxidation reaction. Figures 7 through 16 show the carbon and oxygen contents as a function of treatment time for the runs made using the Group IV operating procedure. The oxygen content vs. time curves are shown with a cusp; the upper half of which is shown as a dotted line. The reason for this particular method of presentation can be found by considering the experimental procedure. Each charge for this particular series of runs was melted under a carbon monoxide pressure of 600 mm Hg. and was held at this pressure for 30 min. The results of run 11 indicate that within the 30 min. time period the oxygen content of each melt approachs a constant or "equilibrium" value. This approach to oxygen content "equilibrium" is shown in Figures 7 through 16 as the dotted segment of the curve.

After a sample had been obtained at the end of 30 min. at 600 mm Hg. of carbon monoxide, the chamber pressure was rapidly reduced to a new pressure level. The oxygen content of the bath reacts to this pressure change by approaching a new constant or "equilibrium" value. Thus the second segment of the curve is drawn to show the approach to the new "equilibrium" oxygen value.

The carbon contents for all runs can be seen to exhibit a steady decrease with treatment time. This decrease, however, does not appear to be dependent upon chamber pressure nor upon a particular chamber pressure as duplicate pressure runs always exhibited different carbon content behavior (this point will be discussed in greater detail later).

Pressure Dependency of the Carbon Deoxidation Reaction

The pressure dependency of the carbon-oxygen reaction may be examined in a number of different ways. The first, and perhaps the most direct, is to consider the constant or "equilibrium" oxygen content obtained at each pressure level.

The curves of Figures 7 through 17 indicate that the approach to the "equilibrium" oxygen concentration is quite rapid and generally takes place within the first fifteen minutes at the new pressure level. Therefore, the oxygen analyses for samples B through D can be considered as representative of the "equilibrium" oxygen concentration at a particular pressure level. The average value of these determinations and the standard deviation were computed for each pressure level including 600 mm Hg. The results of this calculation are presented in Table IV and are shown graphically in Figure 18. This figure shows that the oxygen content of a melt rapidly decreases as chamber pressure decreases until a pressure level of approximately 100 mm Hg. is reached. Below the pressure of 100 mm Hg. of carbon monoxide, the change in oxygen concentration with decreasing chamber pressure is not significant, as the "equilibrium" oxygen contents at the lower pressures fall within a range of 20 to 30 ppm. It is interesting to note that the "equilibrium" oxygen contents for runs 4 through 9 also fall within this range. This indicates that these values represent true "equilibrium" values and are not dependent upon operational technique.

Another method of assessing the pressure dependency of the carbon deoxidation reaction is to consider the percent reduction in the initial oxygen content as a function of the treatment pressure. Table V and Figure 19 show the results of this analysis. Two methods of calculation were utilized for the determination of percent oxygen removed. One method is based upon the calculated oxygen content of the initial charge material (162 ppm), while the other is based upon the individual run, average oxygen content for the equilibration period of 600 mm Hg. of carbon monoxide. This way of presenting the data again illustrates the fact that no significant change in oxygen removal is produced by vacuum treatment at pressures less than approximately 100 mm Hg.

The carbon deoxidation reaction in molten iron may be expressed by the following equation:

$$\underline{C} + \underline{O} = CO(g) \tag{1}$$

The pressure dependency of the reaction is demonstrated by a consideration of the thermodynamic equilibrium constant for the reaction:

$$K = \frac{P_{co}}{h_c h_o} \tag{2}$$

where K is the thermodynamic equilibrium constant, P_{co} is the partial pressure of carbon monoxide at equilibrium, and h_c and h_o are the Henrian activities of carbon and oxygen, respectively, in molten steel.

The value of K has been determined experimentally. After a consideration of the available data, it appears that the expression given by Bennett and coworkers[11] represents the best value. This expression, given as a function of temperature, is

$$\log K = + \frac{1045}{T} + 2.131 \tag{3}$$

Substitution of the temperature utilized in this study (2880°F) into expression (3) yields a value for K of 495.

The Henrian activities can be calculated from the experimental carbon and oxygen values using the Henrian activity coefficients for carbon and oxygen. These, in turn, are calculated using the Henrian activity interaction coefficient f_j^i, which accounts for the influence of element i upon element j in solution in molten iron alloys. Thus

$$h_c = (\text{wt. pct. } \underline{C})\, f_c \tag{4}$$

and

$$h_o = (\text{wt. pct. } \underline{O})\, f_o \tag{5}$$

where

$$f_c = f_c^{\,c} \times f_c^{\,o} \tag{6}$$

and

$$f_o = f_o^{\,o} \times f_o^{\,c} \tag{7}$$

Values for f_j^i can be obtained by the use of the following expression:

$$\log f_j^i = e_j^i \text{ (wt. pct. j)} \tag{8}$$

where e_j^i is an experimentally determined interaction coefficient.

The recent work of Ban-ya and Matoba[5] on carbon-oxygen equilibrium includes expressions for $\log f_j^i$ which are compatible with previously published data. These expressions are:

$$\log f_C^C = 0.298 \text{ (wt. pct. } \underline{C}) \tag{9}$$

$$\log f_C^O = -0.316 \text{ (wt. pct. } \underline{O}) \tag{10}$$

$$\log f_O^O = -0.20 \text{ (wt. pct. } \underline{O}) \tag{11}$$

$$\log f_O^C = -0.421 \text{ (wt. pct. } \underline{C}) \tag{12}$$

Expressions (2) through (12) can be used with the appropriate experimental data of this study to calculate any of the carbon-oxygen reaction parameters shown in expression (2), i.e., K, P_{CO}, or the carbon-oxygen product. These calculated values then can be compared with the experimentally obtained values.

Bennett, Protheroe, and Ward[11] suggest that a convenient method of assessing the efficiency of carbon deoxidation is to consider the equilibrium carbon monoxide partial pressure, P_{CO}, obtained from expression (2) by the use of the proper value of K. As the value of P_{CO} decreases, the efficiency of deoxidation increases. It is stated that this procedure avoids the difficulty in comparison of oxygen contents at different carbon levels. The calculation of P_{CO} and its use as a measure of deoxidation efficiency is particularly appropriate in the present study as the chamber pressure is maintained by carbon monoxide. Therefore, calculations were made to determine the theoretical partial pressure of carbon monoxide for each experimental pressure level. In each case, the oxygen cont utilized was the average value shown in Table IV. The carbon content utilized in all but one case was that obtained on the D sample. This lone exception was the 600 mm Hg. pressure level, where the carbon content utilized was the average value obtained from run 11 and all A samples of the Group IV runs. The average value in this latter case was 0.19 pct. with a standard deviation of ±0.01 pct. The results of the calculations are given in Table VI. These calculated P_{CO} values can be compared with the actual chamber pressure using Figure 20.

It can be seen that at the measured chamber pressure of 600 mm Hg., the calculated pressure, i.e., 608 mm Hg. shows excellent agreement with the measured pressure. This indicates that at 600 mm Hg. the system is governed by thermodynamic equilibrium consideration. As the chamber pressure is reduced below 600 mm Hg. the calculated partial pressure begins to deviate from the experimental pressure. At a chamber pressure of 200 mm Hg. of CO, the deviation amounts to approximately 140 mm Hg. This behavior may indicate that true thermodynamic equilibrium for the reaction expressed by equation (1) may not be attained at chamber pressures less than 600mm Hg. The exact pressure level for the start of deviation was not established in the present study, as no runs were conducted at pressures between 600 and 200 mm Hg. It will be observed from Table VI that at chamber pressures of 200 mm Hg., or less, the deviation between calculated and experimental partial pressures of carbon monoxide ranges from 97 mm to 146 mm Hg., with an average value of 127mm Hg.

If the theoretical partial pressure of carbon monoxide is used as a measure of deoxidation efficiency, then it appears that for an actual chamber pressure somewhere below 600 and above 200 mm Hg., carbon deoxidation becomes theoretically inefficient from a thermodynamic standpoint. It is interesting to note that Bennett and coworkers[11] obtained deviations of 118 mm Hg. in their work which was conducted at chamber pressures of 1-2 microns.

Although the use of thermodynamic considerations points out that carbon deoxidation becomes inefficient at a very high reduced pressure, it can be seen from Figures 18 and 19 that a significant amount of oxygen removal takes place at chamber pressures between 200 and 100 mm Hg. In fact, it is not until chamber pressures of less than 100 mm Hg. are reached that the oxygen content fails to exhibit significant changes as a function of pressure.

A possible explanation for the differences between the theoretical and experimental assessment of efficiency may be found by considering the expression for the equilibrium constant given by equation (2). Meadowcroft[16] points out that the carbon monoxide term appearing in the expression for the equilibrium constant is the partial pressure of carbon monoxide in the gas bubbles forming within the melt and not the pressure of the gas phase at the melt surface. This statement should be corrected to state that the carbon monoxide term is not necessarily the external gas pressure.

The equilibrium partial pressure inside a bubble which forms heterogeneously at reaction sites located at the melt-refractory interface may be expressed by:

$$P = P_{ex} + P_{melt} + P_{bubble} \qquad (13)$$

where

P_{ex} = the chamber pressure,

P_{melt} = pressure due to the ferrostatic load of the melt, density x gravity x melt depth, and

P_{bubble} = pressue due to bubble surface pressure, 2 x interfacial tension/ bubble radius.

Meadowcroft states that "only if the equilibrium CO pressure of the melt exceeds the value of P will bubbles be nucleated and the boil sustained."

Using expression (13), published data, and the experimental results of this study, it can be seen that the external chamber pressure is the dominate pressure term above approximately 600 mm Hg. This, then, indicates that the utilization of the chamber pressure in the equilibrium constant expression will not cause serious errors at pressures greater than 600 mm Hg. Below 600 mm Hg. chamber pressure, the influence of the chamber pressure decreases to such a degree that the melt and bubble pressures become the governing factors. Using the approach of nucleation of suitably sized bubbles, Meadowcroft predicts that carbon deoxidation becomes inefficient at chamber pressures less than approximately 7.6 mm Hg. at which point the carbon boil should cease.

Visual observations of the melt surfaces during this study revealed that a carbon boil* does not occur until the chamber pressure was reduced to values below 10 mm Hg. In other words, a quiescent melt surface was observed for all Group IV runs when the chamber pressure

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* A carbon boil is here defined as the case where the melt surface is disrupted by bursting gas bubbles.

exceeded 10 mm Hg. It is interesting to note further that the quiescent melt conditions produced the greatest amount of oxygen removal. This fact appears to indicate that oxygen removal is being accomplished by the surface desorption of carbon monoxide. In the cases where a carbon boil was observed, it was noted that the boil was sustained for only a short time before quiescent conditions were established. The observance of two mechanisms for the removal of oxygen is in accord with Machlin's theory of vacuum induction refining[9].

Despite the fact that a carbon boil is observed at lower treatment pressures, the experimental results show that oxygen removal is not particularly enhanced. This and the other items mentioned previously suggest that the oxygen values obtained for the lower operating pressures are not true thermodynamic equilibrium values, but rather are steady-state values resulting from a balance between oxygen removed from the melt by deoxidation reactions and oxygen fed to the melt by a reaction between the melt and the crucible material.

Melt-Crucible Reaction

The existence of a melt-crucible reaction during vacuum treatment was acknowledged during the establishment of the experimental program. It was hoped that this reaction could be evaluated as a function of treatment pressure and time by the use of high purity alumina crucibles.

A possible reaction for alumina and carbon dissolved in molten iron is:

$$Al_2O_3(s) + 3\underline{C} = 2\underline{Al} + 3CO(g) \qquad (14)$$

The extent of such a reaction should be demonstrated by an increase in the aluminum content of the melt. In addition, the amount of carbon consumed by the reaction can be calculated and compared with that obtained experimentally. The aluminum analyses for the experimental runs may be found in Table III. It was found during the course of the experimental program that the addition of a small amount of aluminum wire was required for each sample mold in order to insure a sound casting for oxygen analysis. Therefore, the analytical results should give values which include the aluminum content intentionally added plus the aluminum content from the crucible reduction reaction. A comparison of the deliberate aluminum content with the analyzed aluminum content, as shown in Table III, shows that, in many cases, it is difficult to account for the deliberate addition let alone the aluminum which theoretically should be picked up from the crucible.

In the cases where the analyzed aluminum content is greater than that expected from the deliberate addition, it will be noticed that the difference between the analyzed amount and deliberate addition is often insufficient to account for the theoretical aluminum content calculated from reaction (14) and the observed carbon drop. The reason for these apparent differences in aluminum content has not been determined, but may be due to errors in sampling procedure, sample cutting practice, float out, segregation, or analytical procedures. An additional source of the difference in the aluminum values was thought to be the fact that the aluminum generated by the reaction might not be retained in the melt.

The existence of some dissolved aluminum in the melt was demonstrated by run 26. After the equilibration period at 600 mm Hg. of carbon monoxide, the chamber pressure was reduced to 20 mm Hg. and held for 30 min. The chamber pressure was then increased to 200 mm Hg. by the introduction of carbon monoxide. As soon as the gas was bled into the chamber, a crust was observed to form on the bath surface. This alumina crust, which was formed by the reaction of dissolved aluminum and the carbon monoxide atmosphere, has been observed under similar circumstances by Parlee and coworkers[19]. Run 26 thus provided a qualitative demonstration of dissolved aluminum.

Inspection of reaction (14) shows that while the reaction can be utilized to account for the consumption of carbon during processing, it does not account for the pick up of oxygen by the melt. In order for reaction (14) to furnish oxygen to the melt, the carbon monoxide generated would have to become dissolved in the melt. It should, however, be pointed out that the carbon monoxide is being generated in an area where it is believed that carbon monoxide bubbles are easily nucleated, i.e., the pores in the refractory surface. Thus, any carbon monoxide generated should be removed from the melt.

On the basis of the above considerations, it appears that reactions other than reaction (14) should be considered for the melt-crucible interaction. Examples of melt-crucible reactions which could account for the feeding of oxygen to the bath and the observed aluminum contents have been given by Meadowcroft and Elliott[15] and are discussed below.

The simplest type of reaction to consider is one in which the crucible refractory decomposes to form either two gaseous reaction products, one gaseous and one dissolved reaction product, or two dissolved reaction products. Examples of some of these reactions for alumina crucibles are given below:

$$Al_2O_3(s) = 2\underline{Al} + 3\underline{O} \qquad (15)$$

$$Al_2O_3(s) = 2Al(g) + 3\underline{O} \qquad (16)$$

$$Al_2O_3(s) = 2AlO(g) + \underline{O} \qquad (17)$$

$$Al_2O_3(s) = Al_2O(g) + 2\underline{O} \qquad (18)$$

All of the above reactions can account for oxygen pick up by the melt. Reactions 16 through 18 can also account for the failure to find sufficient amounts of aluminum dissolved in the melt to account for the observed carbon drops. The oxygen liberated by the reactions can diffuse to the melt surface where the formation and surface desorption of carbon monoxide is possible.

Another type of reaction for consideration involves the reduction of alumina with iron. Examples for such reactions are shown below:

$$3/2\ Fe(\ell) + 1/2\ Al_2O_3(s) = 3/2\ FeO(\ell) + Al(g), \qquad (19)$$

$$P_{Al} = 3.2 \times 10^{-9} atm$$

$$1/2\ Fe(\ell) + 1/2\ Al_2O_3(s) = 1/2\ FeO(\ell) + AlO(g), \qquad (20)$$

$$P_{AlO} = 4 \times 10^{-10} atm$$

$$2\ Fe(\ell) + Al_2O_3(s) = 2\ FeO(\ell) + Al_2O(g), \qquad (21)$$

$$P_{Al_2O} = 4 \times 10^{-10} atm$$

These reactions again provide a means of supplying oxygen to the melt by solution of FeO and of removing aluminum from the bath as a gaseous specie. It will be noted that the partial pressures of the various gaseous aluminum species are considerably lower than the prevailing chamber pressure for any given experimental run. However, it should be pointed out that the partial pressure is that in the reaction zone. A build up in the gaseous species in the reaction zone is prevented by the induction stirring action of the bath and by the diffusion of the species from the reaction zone into the bulk of the melt. Both items would effectively lower the partial pressure of the gaseous species so that the reaction or reactions could proceed. The loss in carbon content of the melts can be explained by the subsequent reduction of the FeO by dissolved carbon to form carbon monoxide. The reaction with carbon could occur at either the refractory interface or the melt surface.

The reactions 14 through 21 provide possible explanations for the behavior of the experimental data. However, they also point out the impossibility of determining either the exact reaction or the extent each reaction participates in the overall melt-crucible reaction. The analytical procedures for aluminum are somewhat difficult and, therefore, it would appear desirable to analyze the experimental data using the carbon content of the melt, since this is a more easily and accurately determined quantity.

The removal of carbon from the bath can be accomplished only by the combination with oxygen to form carbon monoxide as illustrated by equation (1). The amount of carbon consumed by this reaction can be calculated from the amount of oxygen removed by the stoichiometric factor $\frac{12}{16}$. Using the calculated starting oxygen content of 162 ppm and the average oxygen content obtained at each pressure level, the amount of carbon consumed in each case can be calculated. Since only two place carbon values were reported experimentally, the calculated carbon drops were rounded off to a two place figure. In all cases the amount of carbon consumed in obtaining the observed oxygen contents at the various pressure levels was approximately 0.01 wt. pct. This indicates that the final carbon content for all runs should be 0.20 wt. pct. Table III and Figures 7 through 16 show that for most of the Group IV runs, the final carbon contents are below this calculated final value of 0.20 wt. pct.

The carbon decrease in excess of the calculated value of 0.01 pct. has been tabulated below under the heading of △ carbon.

Run	Final Pressure (mm Hg.)	△ carbon (wt. pct. x 10^2)
11	600	4
12	200	11
14	20	1
15	0.5	4
17	2	8
18	10	6
19	100	0
20	50	3
21	200	2
22	5	4
23	0.5	6
24	0.05	2
25	0.05	5

Inspection of these △ carbon values shows that the values appear to be independent of treatment pressure level and, in fact, to be independent of pressure itself as duplicate runs produced different values for △ carbon. Consideration of the experimental details of each individual run showed that the values for △ carbon were also independent of the hot or cold leak rates obtained for each particular run. These factors tend to indicate that Δ carbon is not dependent upon a measurable experimental quantity.

It was originally planned to limit the experimental program to the investigation of only one variable. In general, this aim was adhered to throughout the course of the program. A noteworthy exception, however, was that the melt size coupled with the chamber geometry resulted in the use of a new alumina crucible for each run. Each of these crucibles was baked in vacuum at elevated temperatures prior to use; however, this treatment is effective only for the removal of moisture and occluded gases. Bosworth[13] has shown that the baking of various crucible materials at elevated temperature in a hydrogen atmosphere will reduce the pick up to oxygen by iron melts. This result is caused by the prereduction of suboxides and impurity oxides. Bosworth's study then indicates that crucibles in the "as-received condition" may not be capable of providing a good melting interface.

Further evidence for the unsuitability of a fresh refractory interface for vacuum work has been reported by Samarin[20] who states that "some three or four heats were made in them (Al_2O_3 crucibles) before the experiments so as to remove the interaction of the crucible with iron containing 0.8-1.0%C."

In view of the above information, it is proposed that the Δ carbon values obtained in this study are a quantitative measure of the overall reactivity of the refractory surface which is in contact with the iron melt. The overall reactivity factor should include such items as the major oxide, impurity oxides, location of the impurity oxides in relation to the melt-crucible interface, porosity of the refractory material, and the roughness of the crucible surface. As can be seen, several of the items included in this reactivity factor can not be quantitatively determined.

Some support for the utilization of △ carbon as a measure of new crucible reactivity can be found in the work of Winkler[14] on the behavior of various crucible materials in the presence of strong reducing agents. A ball-bearing grade of steel was remelted in fresh crucibles of various compositions and the results were given to show the influence of crucible material upon the final oxygen content obtainable. The new alumina crucible showed a △ carbon value of 6 for the first melt, while the second melt in the same crucible showed a △ carbon value of zero. The difference in oxygen content between melts was only 1 ppm.

The concept of △ carbon as a quantitative measure of new crucible reactivity appears to be a reasonable explanation for the carbon drops observed in this experimental program.

One further item of the experimental data requires an explanation. Although analyses obtained on E sample material generally did not agree with the results obtained on A through D samples, the aluminum analyses for runs 15 through 25 show an interesting trend. The analyses can be divided into two groups; namely, those samples which contain less than 0.005 wt. pct. Al and those samples which contain an average Al content of approximately 0.030 wt. pct. The low aluminum samples were obtained on runs made at final pressures of 100 and 50 mm Hg., while the 0.030 wt. pct. aluminums were obtained on runs made at final pressures of less than 10 mm Hg. This behavior indicates the possibility of a pressure dependency for the reduction or dissociation of the alumina refractory. It would appear that the pressure dependency is in accord with the thermodynamic calculations of Schaffer[18] who, using reaction 14, calculates a critical pressure of 16.9 mm Hg. for alumina in contact with a 0.40 pct. carbon-iron melt.

The △ carbon reactivity concept for a crucible material may be questioned on the basis of these E sample aluminum values. However, the 100mm Hg. figure provides excellent agreement for the concept, since the △ carbon was zero for this particular run. The △ carbon for the other low E sample aluminum contents was 3, but it should be pointed out again that △ carbon is an overall reactivity and takes into account the reduction of impurity oxides, etc. Similar explanations can be made for the runs where the 0.030 wt. pct. aluminum values were observed. It should be pointed out that these more or less constant values may be an indication that the aluminum content is a steady-state value which is obtained by a balance between aluminum being fed from the crucible and aluminum being removed at the bath surface.

The E sample aluminum values suggest another possible explanation. The two more or less constant levels of aluminum may be an indication that different crucible reduction or dissociation reactions are operative in different pressure ranges.

While it was not possible to determine the exact mechanism of the melt-crucible reaction for the experimental results obtained in this investigation, it appears that reaction (14) might be considered as representative of the overall reaction between the iron-melt and the alumina crucible. Hence, reactions 15 through 21 should be considered as possible mechanisms by which the overall reaction is obtained. The combination of the various mechanisms can provide ways of accounting for the pick up of oxygen by the melt, the variation in the aluminum content, and the consumption of carbon.

Comparison of Experimental Data with Industrial Data

As pointed out previously, the industrial results for vacuum carbon deoxidation are not in good agreement with those predicted from theoretical considerations. Therefore, it would be interesting to know if the experimental system and procedure utilized in this study can be used to investigate these areas of disagreement.

A rapid comparison of the experimental results with those obtained on an industrial scale can be made by the use of Figure 1. The average, final carbon and oxygen contents for experimental runs made at CO pressures of 20 mm Hg. or less in this investigation are 0.15 pct. and 0.0024 pct., respectively. From Figure 1, it is found that, industrially, a carbon content of 0.15 pct. results in an oxygen content of approximately 0.0035 pct. The difference between the experimental and industrial values might reflect a superiority of one type of refractory over another, as high purity alumina refractories are not generally utilized in commercial vacuum degassing units.

An additional example of the ability of the experimental system to provide results which are comparable to industrial systems may be found reported in a paper by Sieckman and Schempp[21] on the D-H vacuum deoxidation process. In a trial run for the investigation of carbon deoxidation, the carbon and oxygen content of an unalloyed steel were reduced from 0.20 pct. carbon and 0.0150 pct. oxygen to 0.19 pct. and 0.003 pct., respectively, by a 30 min. treatment at pressures ranging from 500 microns to 10 mm Hg. Similar results can be obtained with the experimental system and procedures of this study.

Therefore, it appears that the experimental system and procedures utilized in this investigation can simulate the results obtained for vacuum carbon deoxidation by industrial degassing systems. This factor should prove to be very beneficial in the solution of many of the problems which exist with the commercial application of vacuum carbon deoxidation.

CONCLUSIONS

The following statements can be concluded from the results of this study:

1. No significant decrease in final oxygen content can be observed at chamber pressures less than 100 mm Hg. of carbon monoxide.

2. The results obtained at 600 mm Hg. of carbon monoxide are in excellent agreement with values calculated from theoretical considerations of the carbon-oxygen reaction. Below chamber pressures of 600 mm Hg., the experimental values show considerable deviation from theoretical values. The amount of deviation does not appear to be pressure dependent. A possible explanation is that the reaction is governed by thermodynamic considerations above 600 mm Hg. and by kinetic considerations at the lower pressures.

3. The final oxygen contents observed for each run are probably not true equilibrium values, but are steady-state values which represent a balance between the oxygen removed from the melt as carbon monoxide and the introduction of oxygen to the melt from the alumina refractory.

4. The final carbon contents of the experimental runs showed erratic behavior. It is thought that the excess carbon consumption represents a measure of the overall reactivity of a fresh crucible surface.

5. Based upon visual observations of the bath during treatment and the final oxygen contents of the various runs, it appears that the bulk of the oxygen removal is accomplished by surface desorption of carbon monoxide and not by a carbon boil.

6. The exact mechanism and extent of the melt-crucible reaction could not be determined in this study.

7. The experimental system and operating procedure can be used to simulate the types of results obtained from industrial vacuum degassing systems for carbon deoxidation.

TABLE I

Chemical Analyses of Experimental Materials

Electrolytic Iron

Element	wt.pct.	Element	wt.pct.
C	.001/.01	Cr	<0.01
Mn	<0.01	Mo	<0.01
P	<0.005	Cu	<0.02
S	0.003	V	<0.01
Si	<0.009	Al	<0.004
Ni	0.05	Sn	0.001
O_2	0.016/0.017		

Carbon-Saturated Iron

Same as above, except C - 4.25 pct.

Crucibles

Constituent	wt. pct.
Al_2O_3	99.01
SiO_2	0.58
Fe_2O_3	0.11
Na_2O	0.17
Other	Balance

Apparent Porosity - 19 pct.

TABLE I (cont'd)

Backing and Topping Material

Constituent	wt. pct.
MgO	72.0
Al_2O_3	27.0
SiO_2	1.4
Fe_2O_3	Trace
B	0.1

TABLE II
HISTORY OF EXPERIMENTAL RUNS

Run No.	Initial Carbon Content, wt. pct.	Temp. °F	Treatment Time min.	Operating Pressure, Gas Species, and Treatment Times for Each Condition	Sampling procedure for Pin-Type Samples. Time taken from Bath Molten	Remarks
1,2,3	0.20	--	--	--	--	Exploratory melts. Many mechanical difficulties.
4	"	2880	65	380 mm Hg. of Ar-29 min. 20 mm Hg. of Ar-36 min.	A-29 min., B-36 min., C-43 min. E-65 mm.*	--
5	"	"	46	380 mm Hg. of Ar-10 min. 20 mm Hg. of Ar-36 min.	A-10 min., B-16 min., C-26 min. E-46 min.*	--
6	"	"	23	20 mm Hg. of Ar-23 min.	A-13 min., E-23 min.*	Turntable mechanism failure. Bridge observed on meltdown.
7	"	"	65	20 mm Hg. of CO-65 min.	A-20 min., B-25 min., C-35 min. D-50 min., E-65 min.*	Bridge observed on meltdown.
8	0.21	"	50	20 mm Hg. of CO-50 min.	A-2 min., B-7 min., C-17 min. D-47 min., E-50 min.*	" " " "
9	"	"	58	20 mm Hg. of CO-58 min.	A-11 min., B-21 min., C-41 min. D-56 min., E-58 min.*	" " " "
10	"	"	60	600 mm Hg. of CO-60 min.	--	Pouring difficulties.
11	"	"	60	600 mm Hg. of CO-60 min.	A-30 min., B-35 min., C-45 min. D-60 min.	--
12	"	"	65	600 mm Hg. of CO-30 min. 200 mm Hg. of CO-35 min.	A-30 min., B-45 min., C-55 min., D-65 min.	--
13	"	--	--	--	--	Vacuum pump failed.

TABLE II (cont'd)
HISTORY OF EXPERIMENTAL RUNS

Run No.	Initial Carbon Content, wt. pct.	Temp. °F	Treatment Time min.	Operating Pressure, Gas Species, and Treatment Times for Each Condition	Sampling procedure for Pin-Type Samples. Time taken from Bath Molten	Remarks
14	0.21	2880	60	600 mm Hg. of CO-30 min. 20 mm Hg. of CO-30 min.	A-30 min., B-45 min., C-60 min.	--
15	"	"	65	600 mm Hg. of CO-30 min. 0.5 mm Hg. of CO-35 min.	A-30 min., B-45 min., C-55 min. D-65 min.	Violent boiling at 10 mm.
16	"	--	--	--	--	Bath froze during run.
17	"	2880	65	600 mm Hg. of CO-30 min. 2 mm Hg. of CO-35 min.	A-30 min., B-40 min., C-55 min. D-65 min.	Furnace trouble. Boil observed.
18	"	"	"	600 mm Hg. of CO-30 min. 10 mm Hg. of CO-35 min.	A-30 min., B-45 min., C-55 min. D-65 min.	No boil observed. Manometer broken.
19	"	"	"	600 mm Hg. of CO-30 min. 100 mm Hg. of CO-35 min.	" " " "	--
20	"	"	"	600 mm Hg. of CO-30 min. 50 mm Hg. of CO-35 min.	" " " "	--
21	"	"	"	600 mm Hg. of CO-30 min. 200 mm Hg. of CO-35 min.	" " " "	--
22	"	"	"	600 mm Hg. of CO-30 min. 5 mm Hg. of CO-35 min.	" " " "	Violent boil observed.
23	"	"	"	600 mm Hg. of CO-30 min. 0.5 mm Hg. of CO-35 min.	" " " "	Thermocouple tube fell into bath. Violent boiling observed upon pouring.

TABLE III (cont'd)
HISTORY OF EXPERIMENTAL RUNS

Run No.	Initial Carbon Content, wt. pct.	Temp. °F	Treatment Time min.	Operating Pressure, Gas Species, and Treatment Times for Each Condition	Sampling procedure for Pin-Type Samples. Time taken from Bath Molten	Remarks
24	0.21	2880	60	600 mm Hg. of CO-30 min. 0.05 mm Hg. of CO-35 min.	A-30 min., B-45 min., C-55 min.	Violent boiling observed when crucible was tilted to start pouring of samples at .05 mm
25	"	"	65	600 mm Hg. of CO-30 min. 0.05 mm Hg. of CO-35 min.	A-30 min., B-45 min., D-65 min.	" " " " "
26	"	"	90	600 mm Hg. of CO-30 min., 20 mm Hg. of CO-30 min., 200 mm Hg. of CO-30 min.	A-30 min., B-50 min., C-75 min. D-90 min.	--

* Obtained from the solidified metal in the crucible.

TABLE III
CHEMICAL ANALYSES OF SAMPLES

Sample No.	Processing Time, min.	wt.pct. C	wt.pct. O	wt.pct. Al Deliberate Addition	wt.pct. Al Analyzed	wt.pct. Si
			GROUPII			
Run No. 4	0	0.20	0.0187	--	< 0.004	<0.009
4A	29	0.11_5	0.0040	0	< 0.003	0.006
4B	36	0.10_5	0.0020	0	< 0.002	0.006
4C	43	0.10	0.0020	0	< 0.002	0.007
4E	65	0.09	0.0020	--	< 0.008	0.007
Run No. 5	0	0.20	0.0187	--	<0.004	< 0.009
5A	10	0.11	0.0070	0.10	0.089	0.009
5B	16	0.10	0.0036	0.10	0.095	0.010
5C	26	0.09	0.0026	0.10	0.108	0.009
5E	46	0.09	0.0022	--	0.100	0.009
			GROUP III			
Run No. 6	0	0.20	0.0187	--	<0.004	<0.009
6A	13	0.16_5	0.0025	0.018	0.017	<0.01
6E	23	0.17_5	0.0021	--	0.005	<0.01
Run No. 7	0	0.20	0.0187	--	<0.004	<0.009
7A	20	0.15_5	0.0030	0.018	0.026	0.017
7B	25	0.15_5	0.0020	0.018	0.021	0.010
7C	35	0.14_5	0.0021	0.018	0.023	0.008
7D	50	0.12_5	0.0017	0.018	0.035	0.012
7E	65	0.10_5	0.0012_5	--	0.051	0.014
Run No. 8	0	0.21	0.0187	--	< 0.004	<0.009
8A	2	0.21	0.0032	0.018	0.016***	0.01
8B	7	0.20	0.0035	0.018	0.005***	0.01
8C	17	0.19	0.0033	0.018	0.017***	<0.01
8D	47	0.18	0.0028	0.018	0.020***	"
8E	50	0.17_5	0.0014	--	-	"
Run No. 9	0	0.21	0.0187	--	<0.004	<0.009
9A	11	0.20	0.0026	0.018	< 0.004***	<0.01
9B	21	0.19	0.0016	0.018	0.007***	"
9C	41	0.17	0.0024	0.018	0.015***	"
9D	56	0.17	0.0023	0.018	0.010***	"
9E	58	0.20_5	0.0012	--	-	"
			GROUP IV			
Run No. 11	0	0.21	0.0162	--	<0.004	<0.009
11A	30	0.20	0.0086	0.056	0.051***	"
11B	35	0.19	0.0087	0.056	0.050***	"
11C	45	0.17	0.0100	0.056	0.015***	"
11D	60	0.15_5	0.0107	0.056	0.026***	"
Run No. 12	0	0.21	0.0162	--	< 0.004	<0.009
12A	30	0.18	0.0107	0.056	0.059***	<0.01
12B	45	0.14	0.0052	0.056	0.049***	"
12C	55	0.11	0.0053	0.056	0.052***	"
12D	65	0.09	0.0062	0.056	0.028***	"

TABLE III (cont'd)
CHEMICAL ANALYSES OF SAMPLES

Sample No.	Processing Time, min.	wt.pct. C	wt.pct. O	wt.pct. Al Deliberate Addition	wt.pct. Al Analyzed	wt.pct. Si
Run No. 14	0	0.21	0.0162	--	<0.004	< 0.009
14A	30	0.20	0.0080	0.056	0.040***	< 0.01
14B	45	0.20	**(0.0047$_5$ (0.0030$_5$	0.014	0.028***	0.01
14C	60	0.19	0.0024	0.014	0.031***	0.01
Run No. 15	0	0.21	0.0162	--	<0.004	<0.009
15A	30	0.19	0.0098	0.056	0.064***	<0.01
15B	45	0.19	0.0035	0.013	0.026***	<0.01
15C	55	0.17	0.0026	0.014	0.020***	< 0.01
15D	65	0.15	0.0028	0.012	0.053***	< 0.01
15E	-	--	--	0.000	0.030	
Run No. 17	0	0.21	0.0162	--	<0.004	< 0.009
17A	30	0.16	0.0107	0.052	0.13	< 0.010
17B	45	0.17	0.0033	0.017	0.022	< 0.010
17C	55	0.14	**(0.0030 (0.0032	0.013	0.037	< 0.010
17D	65	0.12	0.0026$_5$	0.013	0.037	< 0.010
17E	-	--	--	0.000	0.028	
Run No. 18	0	0.21	0.0162	--	< 0.004	< 0.009
18A	30	0.18	0.0093	0.05	0.037	< 0.01
18B	45	0.18	0.0031	0.013	0.053	< 0.01
18C	55	0.16	0.0031	0.012	0.020	< 0.01
18D	65	0.14	0.0023	0.011	0.022	< 0.01
18E	-	--	--	0.000	0.023	
Run No. 19	0	0.21	0.0162	--	< 0.004	< 0.009
19A	30	0.23	0.0087	0.055	0.029	< 0.01
19B	45	0.21	**(0.0049 (0.0032	0.027	0.039-0.067	< 0.01
19C	55	0.21	0.0034	0.026	0.039	< 0.01
19D	65	0.20	0.0030	0.025	0.030	< 0.01
19E	-	--	--	0.000	0.001	
Run No. 20	0	0.21	0.0162	--	< 0.004	< 0.009
20A	30	0.20	0.0095	0.047	0.036	< 0.01
20B	45	0.19	0.0028	0.030	0.045-0.073	< 0.01
20C	55	0.19	0.0030	0.025	0.044	< 0.01
20D	65	0.17	0.0034	0.027	0.039	< 0.01
20E	-	--	--	0.000	0.004	
Run No. 21	0	0.21	0.0162	--	< 0.004	< 0.009
21A	30	0.20	0.0092	0.054	0.072	< 0.01
21B	45	0.19	--	0.028	< 0.001	< 0.01
21C	55	0.17	0.0058	0.033	0.13	< 0.01
21D	65	0.18	0.0048	0.025	0.041	< 0.01

TABLE III (cont'd)
CHEMICAL ANALYSES OF SAMPLES

Sample No.	Processing Time, min.	wt.pct. C	wt.pct. O	wt.pct. Al Deliberate Addition	wt.pct. Al Analyzed	wt.pct. Si
Run No. 22	0	0.21	0.0162	--	< 0.004	< 0.009
22A	30	0.20	0.0085	0.047	0.071	< 0.01
22B	45	0.20	0.0025	0.014	0.034	< 0.01
22C	55	0.18	0.0012	0.012	0.023	< 0.01
22D	65	0.16	0.0019	0.012	0.027	< 0.01
22E	-	--	--	0.000	0.027	
Run No. 23	0	0.21	0.0162	--	< 0.004	< 0.009
23A	30	0.19	0.0096	0.05	0.051	< 0.01
23B	45	0.15	0.0026	0.014	0.039	< 0.01
23C	55	0.16	0.0015	0.014	0.019	< 0.01
23D	65	0.14	0.0022	0.014	0.029	< 0.01
23E	-	--	--	0.000	0.030	
Run No. 24	0	0.21	0.0162	--	< 0.004	< 0.009
24A	30	0.21	0.0084	0.053	0.086	< 0.01
24B	45	0.18	0.0021	0.013	0.013	< 0.01
24C	55	0.18	0.0018	0.014	0.060	< 0.01
24E	-	--	--	0.000	0.028	
Run No. 25	0	0.21	0.0162	--	< 0.004	< 0.009
25A	30	0.19	0.0086	0.049	0.101	< 0.01
25B	45	0.17	0.0024	0.014	0.035	< 0.01
25C	65	0.15	0.0019	0.012	0.031	< 0.01
25E	-	--	--	0.000	0.028	
			GROUP V			
Run No. 26	0	0.21	0.0162	--	< 0.004	< 0.009
26A	30	0.17	0.0087	0.052	0.072	< 0.01
26B	50	0.15	0.0023	0.052	0.089	< 0.01
26C	75	0.15	0.0023	0.057	0.075	< 0.01
26D	90	0.16	0.0024	0.051	0.065	< 0.01

** Two averages reported because oxygen analyses on different portions of the sample pin did not agree.

*** Spectrographic analysis.

TABLE IV

Average Oxygen Concentrations

Carbon Monoxide Pressure, mm Hg.	Average Oxygen Concentration, weight per cent
600	0.0093 ± 0.0010
200	0.0054 ± 0.0006
100	0.0032 --
50	0.0031 ± 0.0006
20	0.0024 ± 0.0006
10	0.0028 ± 0.0006
5	0.0018 ± 0.0006
2	0.0029 ± 0.0006
0.5	0.0025 ± 0.0007
0.05	0.0020 ± 0.0003

TABLE V

Percent Oxygen Removed

Carbon Monoxide Pressure, mm Hg.	Percent Oxygen Removed	
	Based on 162 ppm	Based on Oxygen Content for Individual Heats
600	43	--
200	67	45
100	80	63
50	81	67
20	85	70
10	83	70
5	89	79
2	82	73
0.5	85	74
0.05	88	75

TABLE VI

Comparison of Experimental and Calculated Partial Pressures of Carbon Monoxide

Experimental Pressure of CO, mm Hg.	Calculated Pressure of CO, mm Hg.
600	608
200	339
100	225
50	186
20	166
10	135
5	102
2	127
0.5	141
0.05	109

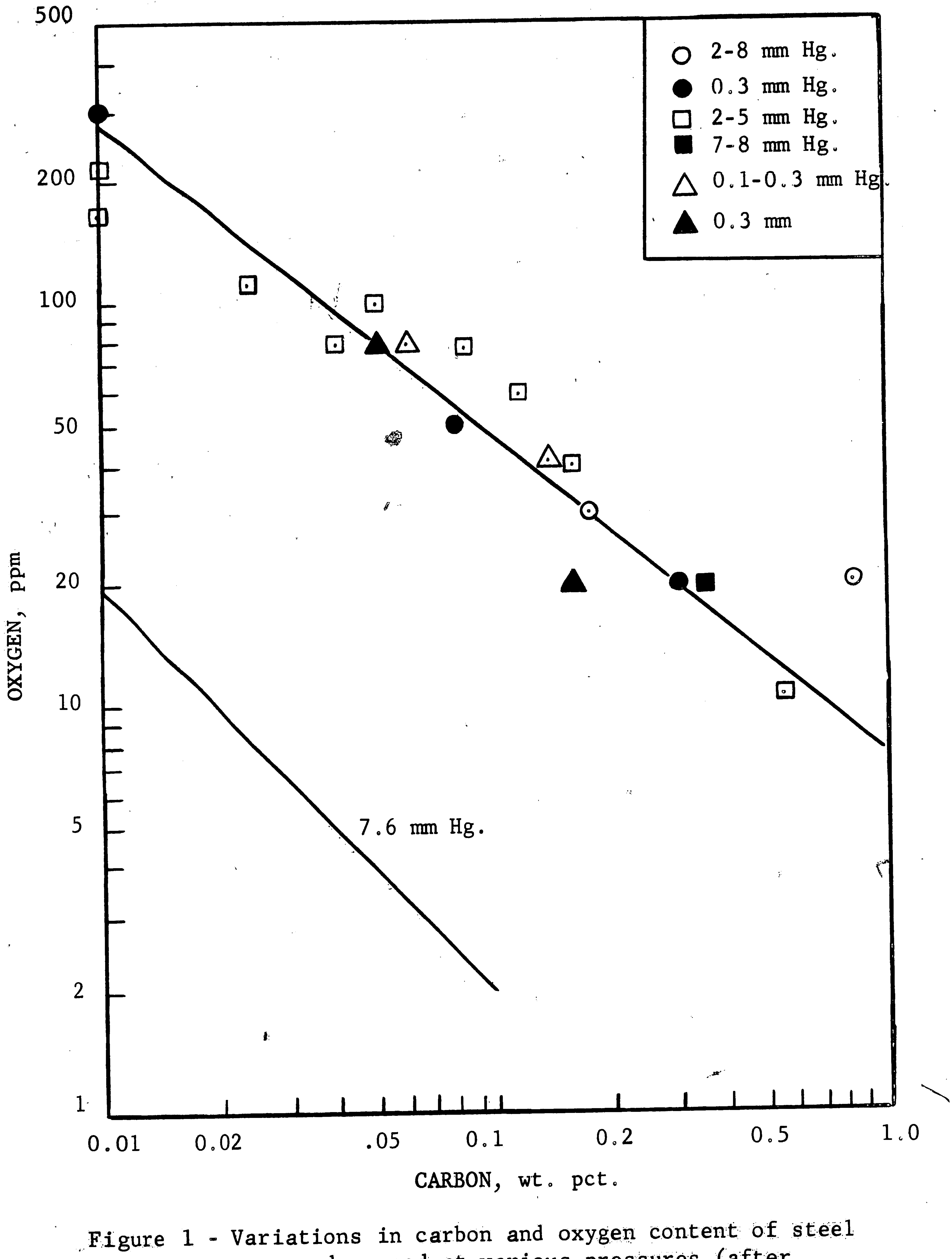

Figure 1 - Variations in carbon and oxygen content of steel vacuum degassed at various pressures (after Hornak[2]).

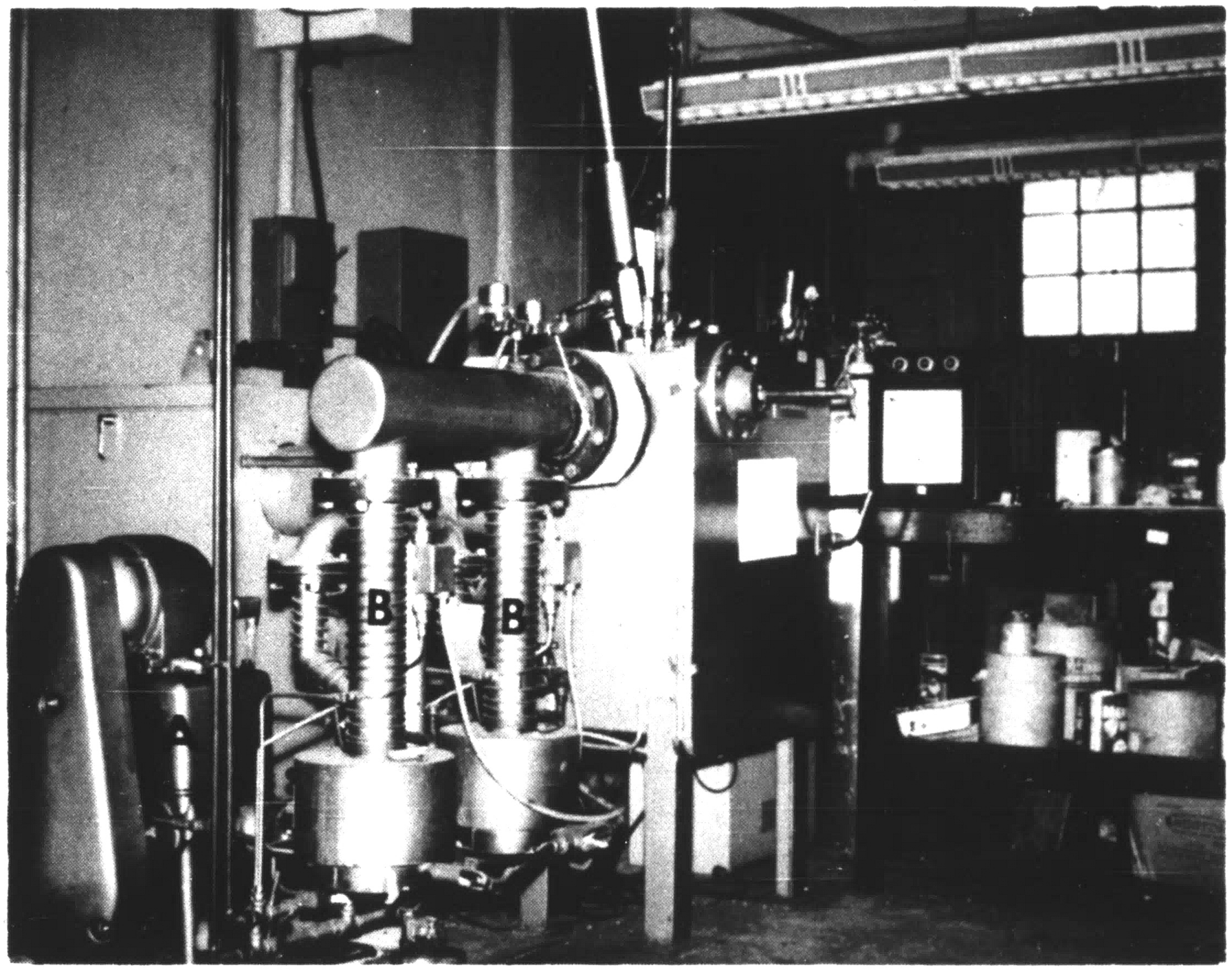

Figure 2 - A View of the Vacuum Pumping Equipment

A. 80 cfm Mechanical Pump

B. 4 in. Diffusion Pump

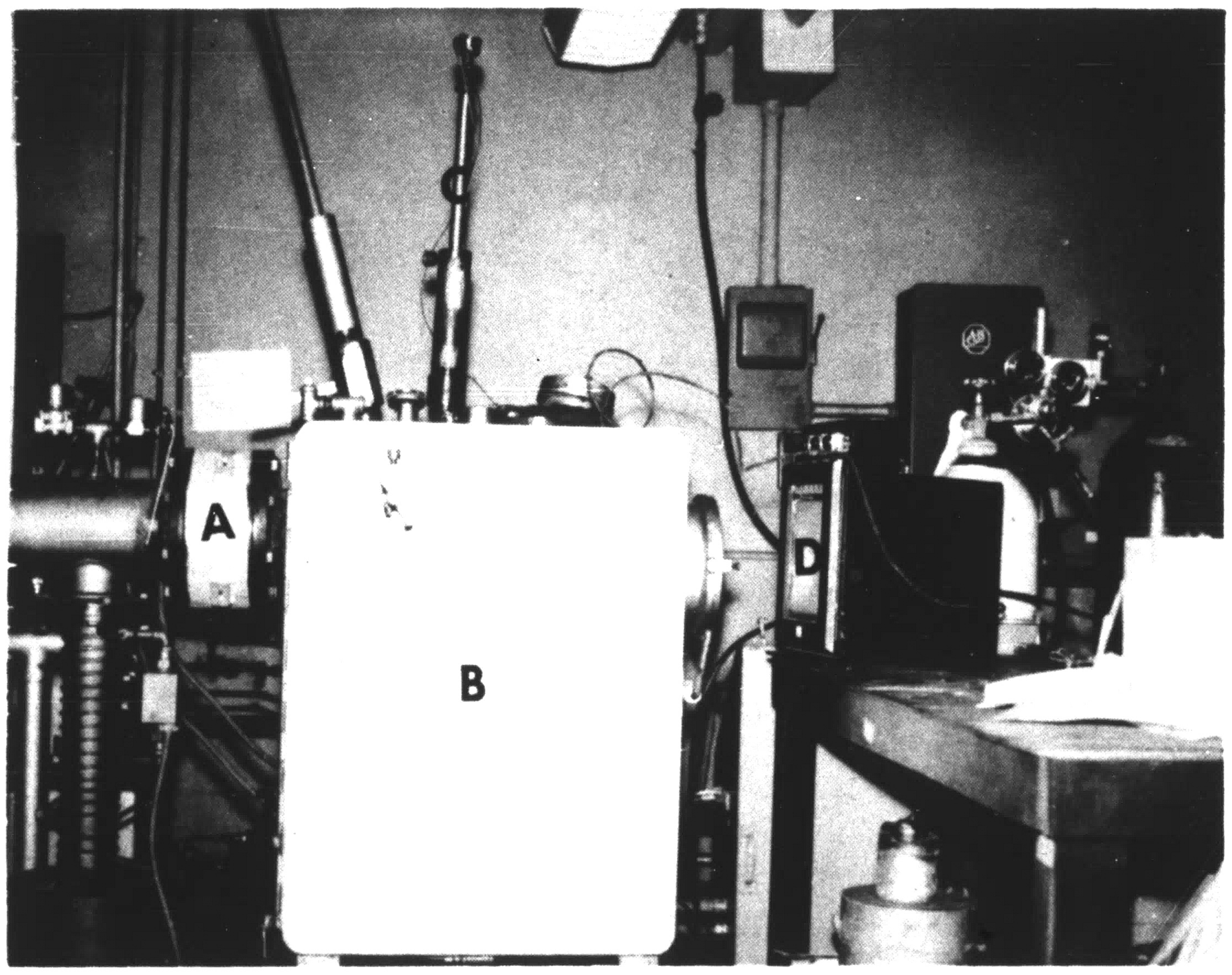

Figure 3 - A View of the Vacuum Chamber

A. 6 in. Gate Valve

B. Vacuum Chamber

C. Thermocouple Probe

D. L and N Speedomax Temperature Recorder

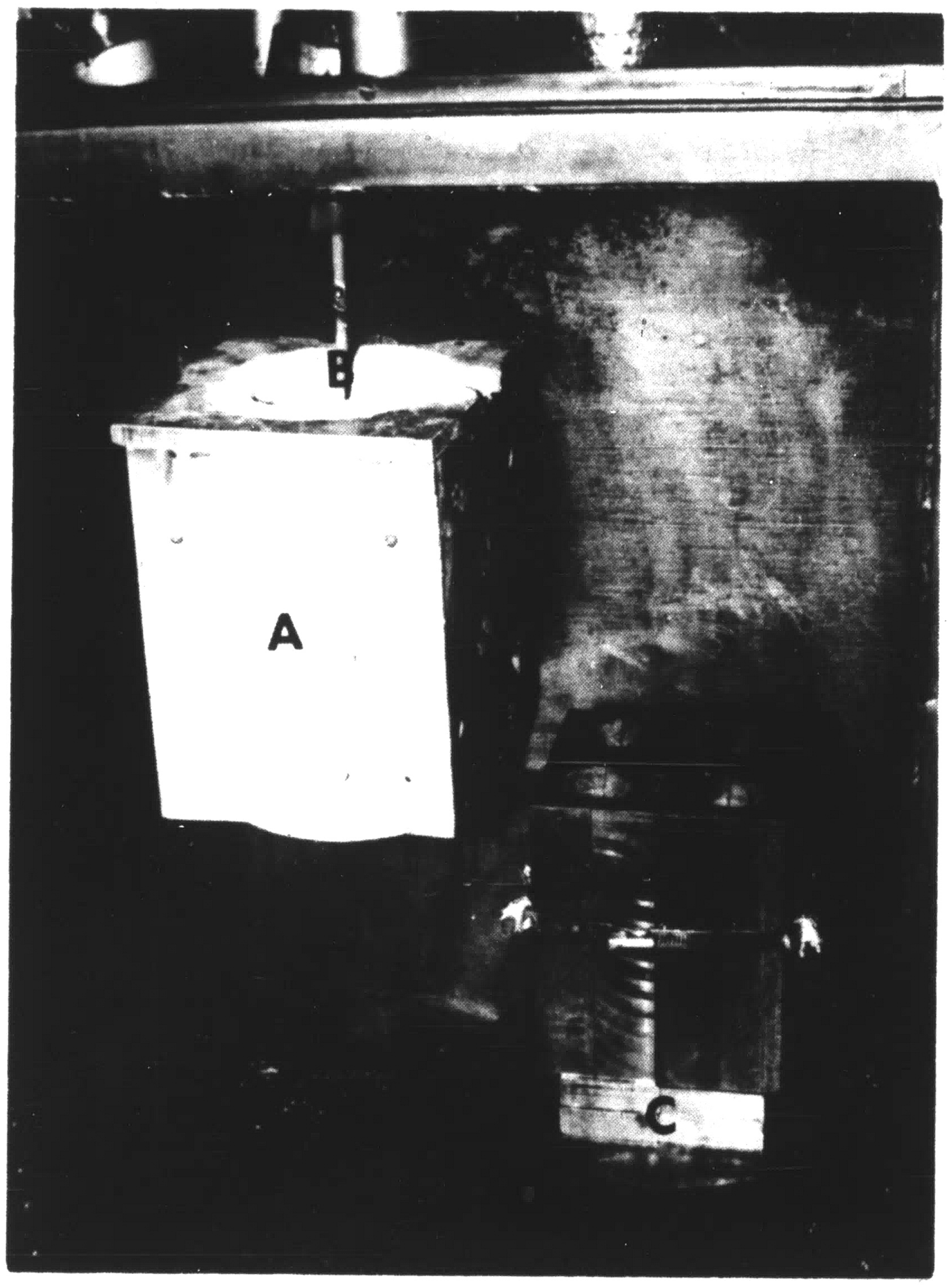

Figure 4 - A View of the Interior of the Vacuum Chamber

A. Induction Furnace Assembly

B. Thermocouple

C. Sampling Molds

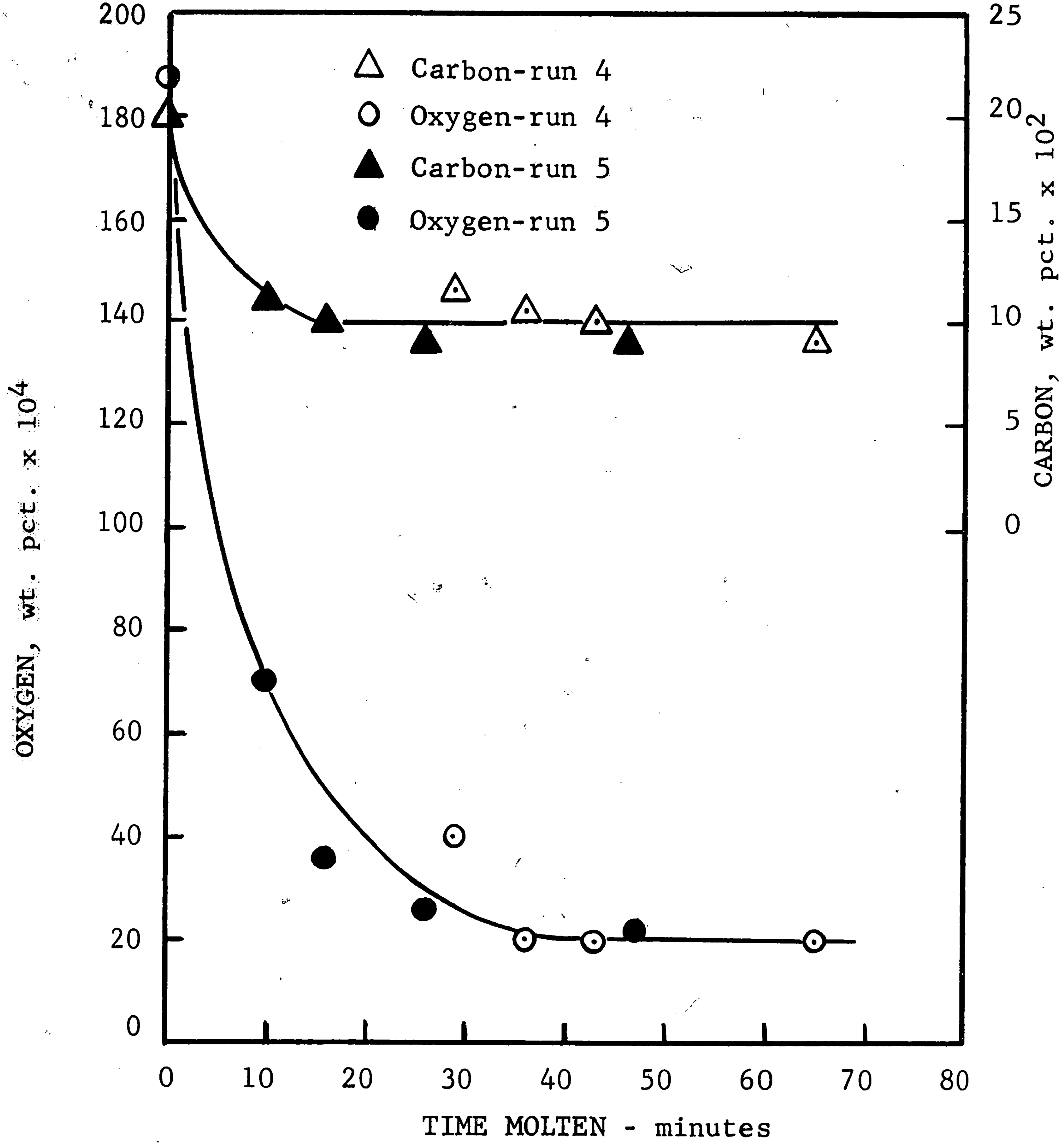

Figure 5 - Variations in carbon and oxygen content of an initially 0.20 wt. pct. C steel with time. Charge was melted under 1/2 atm. of argon and then treated at 20 mm Hg. of argon (runs 4 and 5).

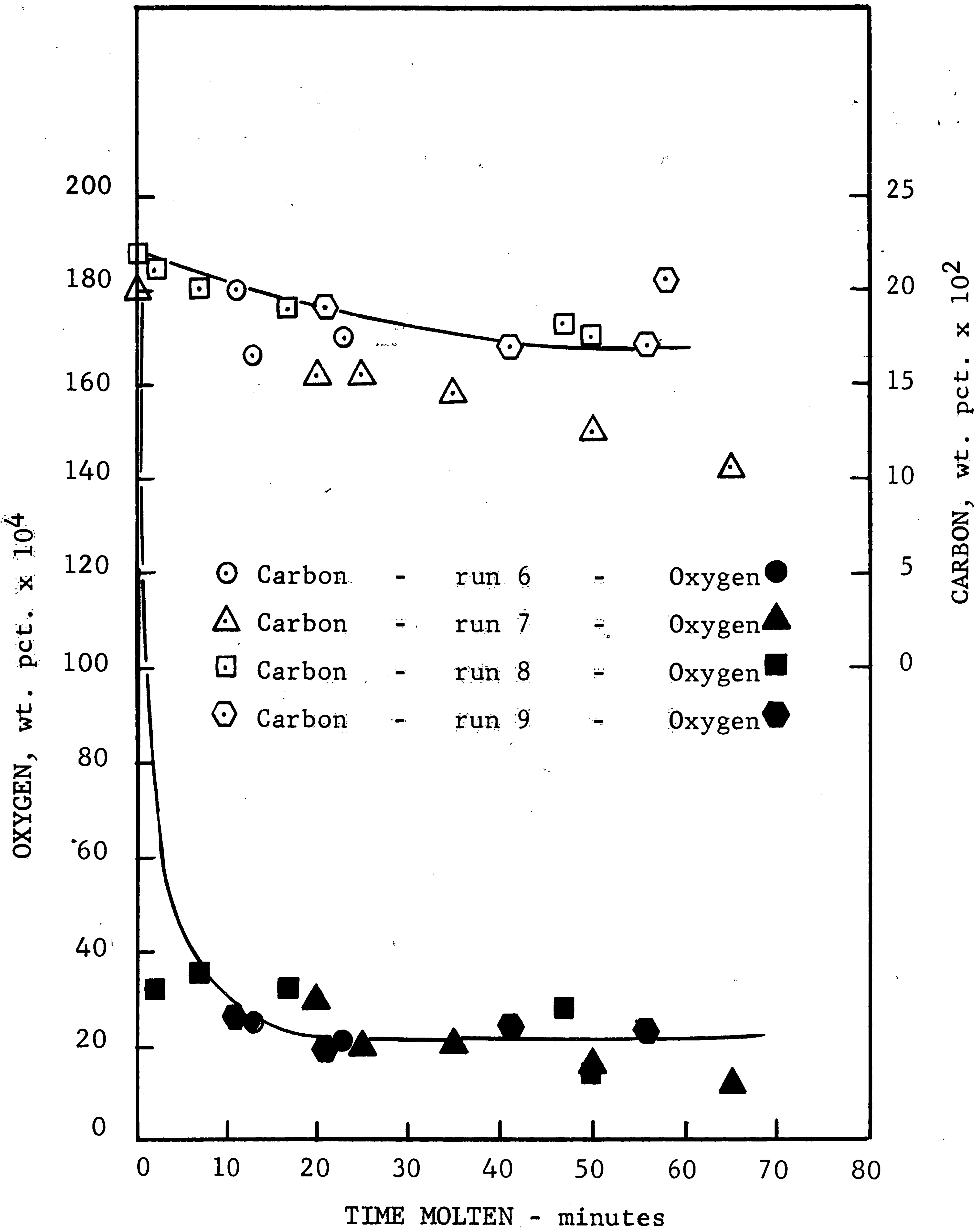

Figure 6 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and treated at 20 mm Hg. of carbon monoxide (runs 6, 7, 8, and 9).

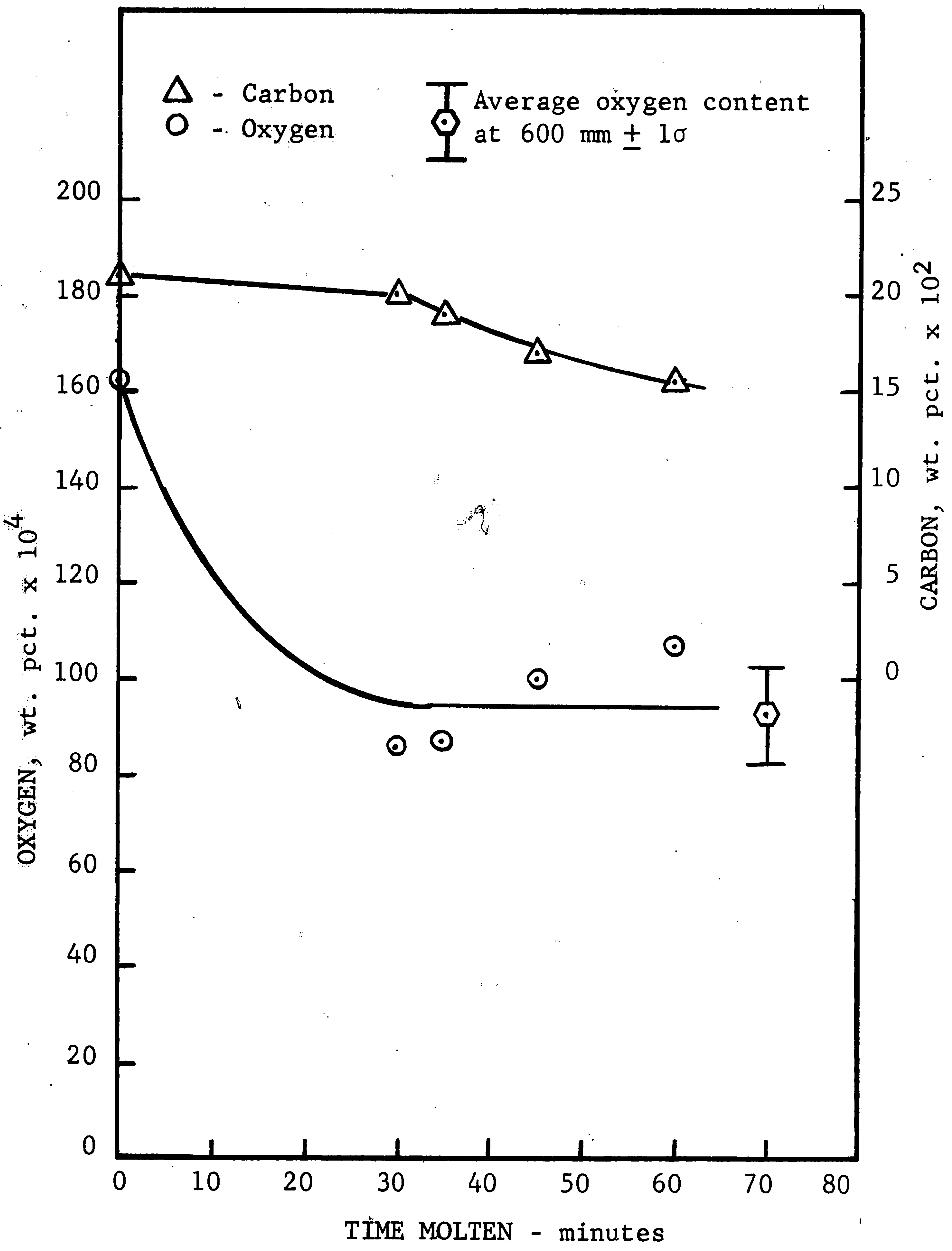

Figure 7 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 600 mm Hg. of CO (run 11).

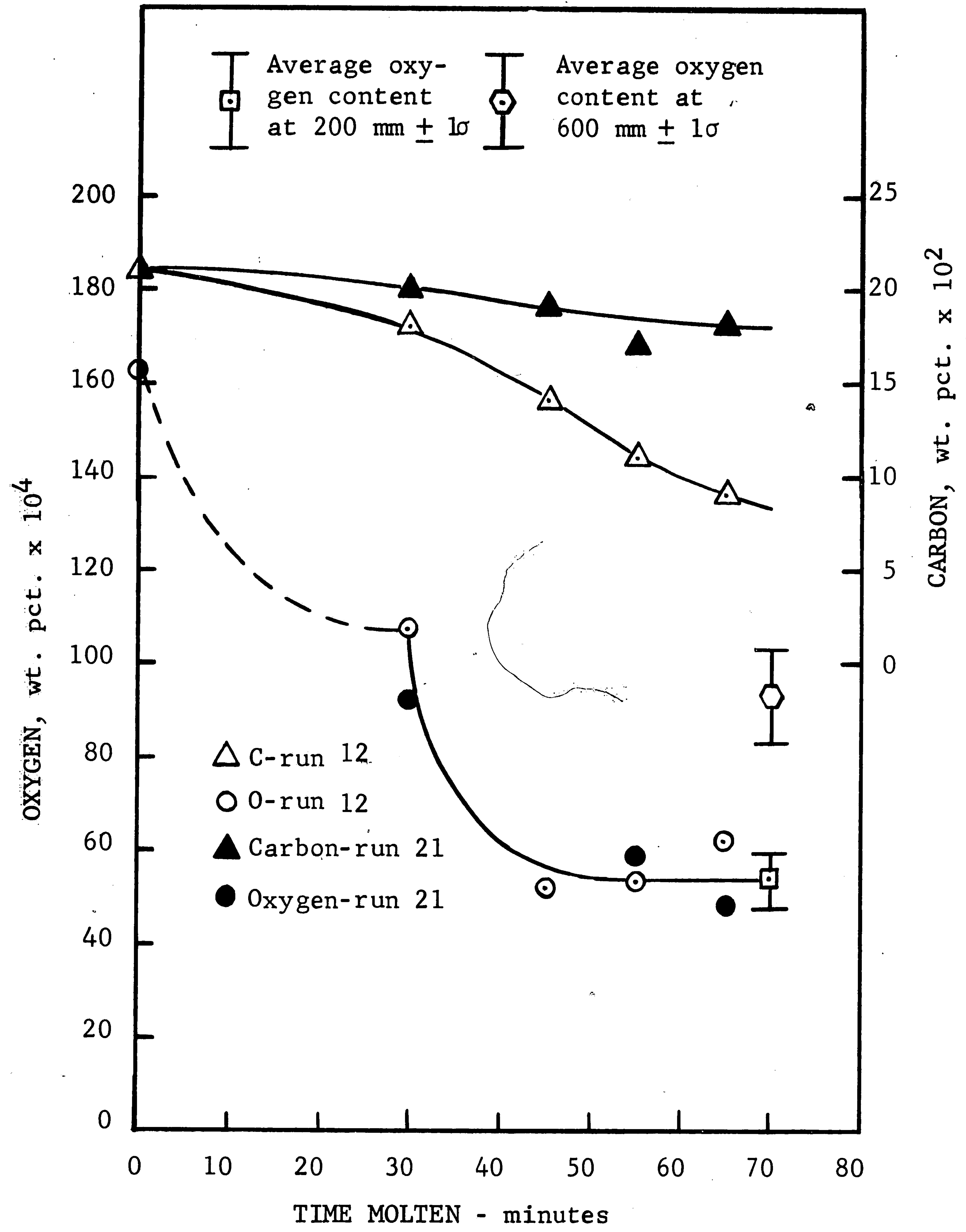

Figure 8 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 200 mm Hg. of CO (runs 12 and 21).

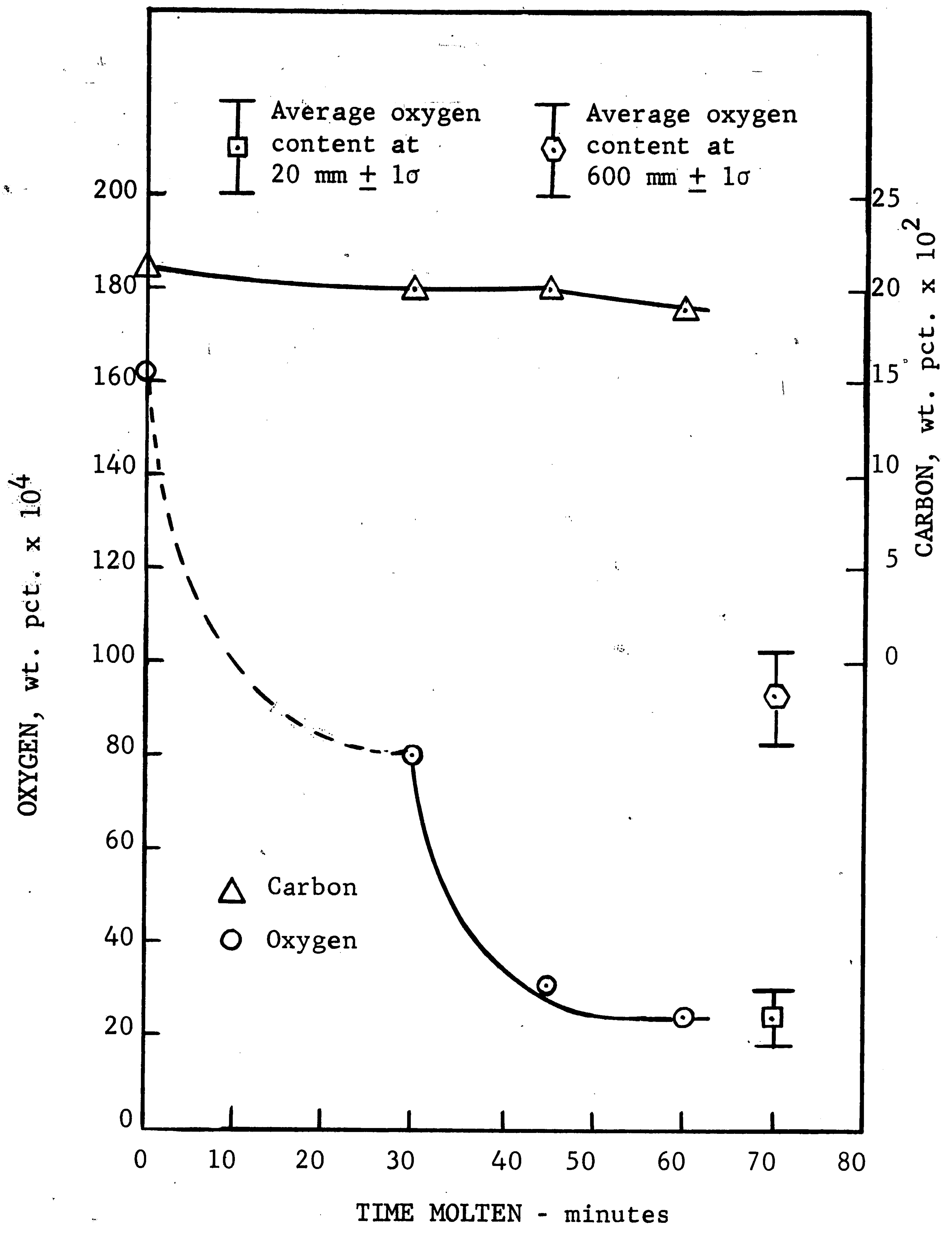

Figure 9 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 20 mm Hg. of CO (run 14).

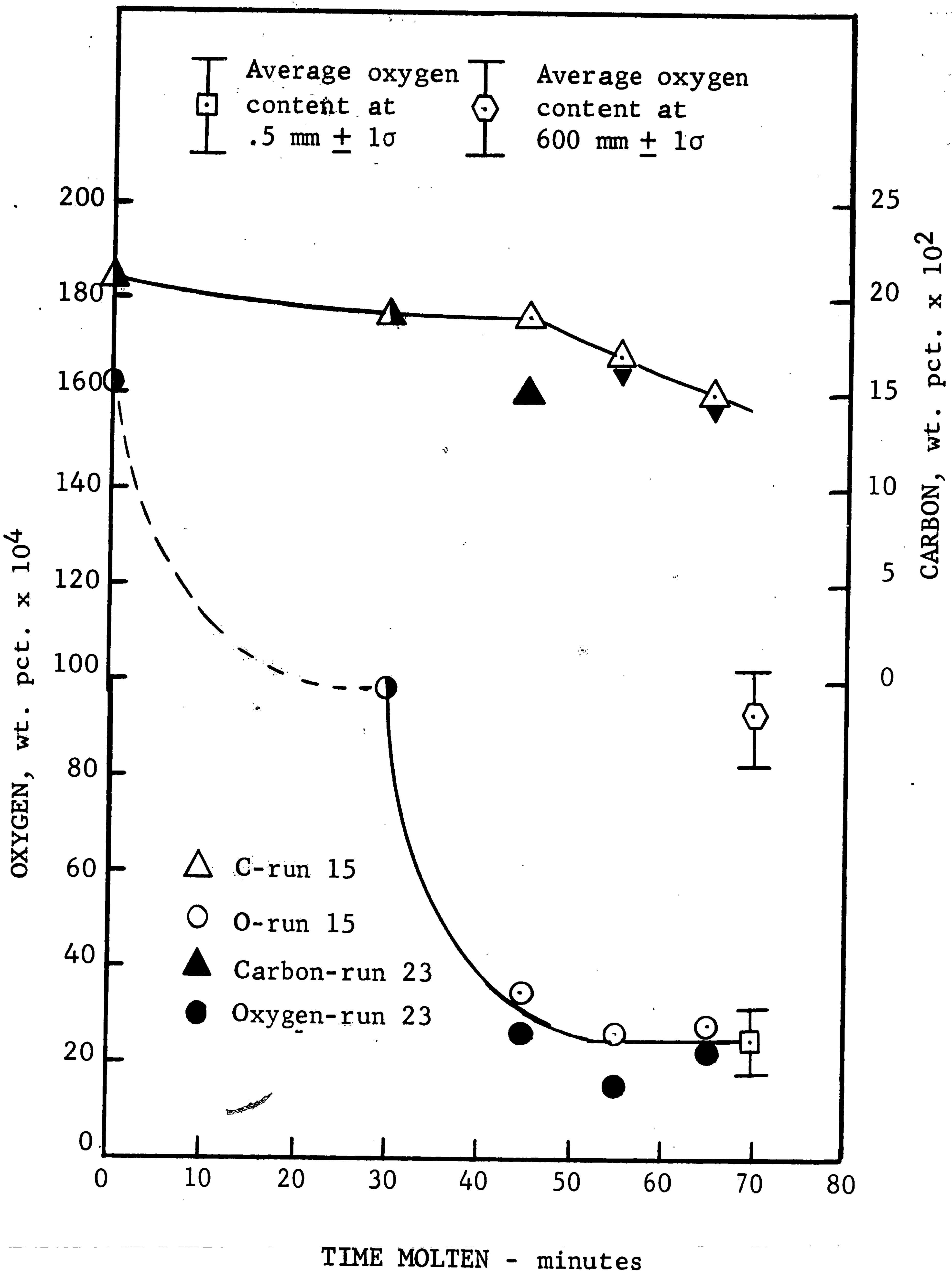

Figure 10 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 0.5 mm Hg. of CO (runs 15 and 23).

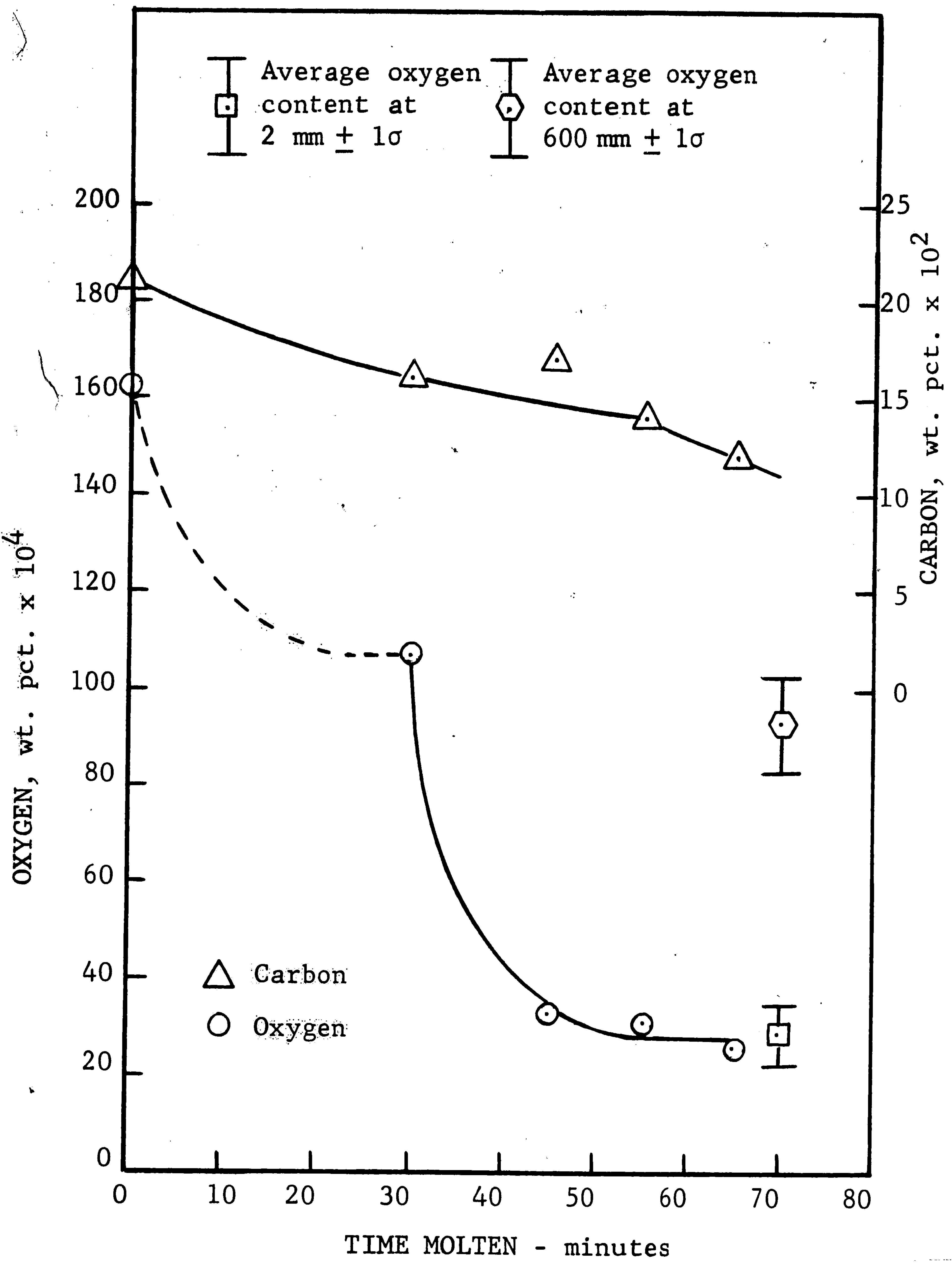

Figure 11 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 2 mm Hg. of CO (run 17).

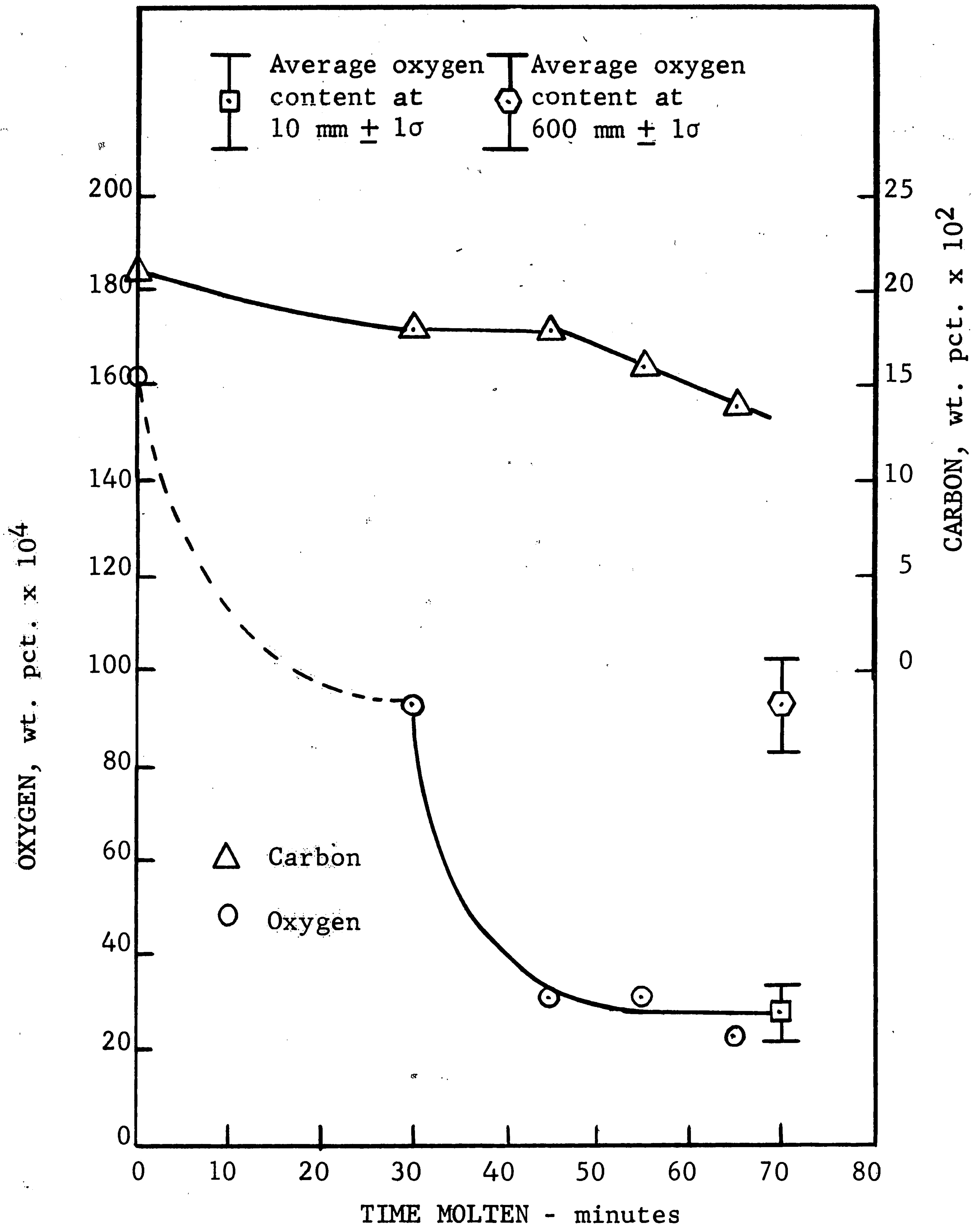

Figure 12 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 10 mm Hg. of CO (run 18).

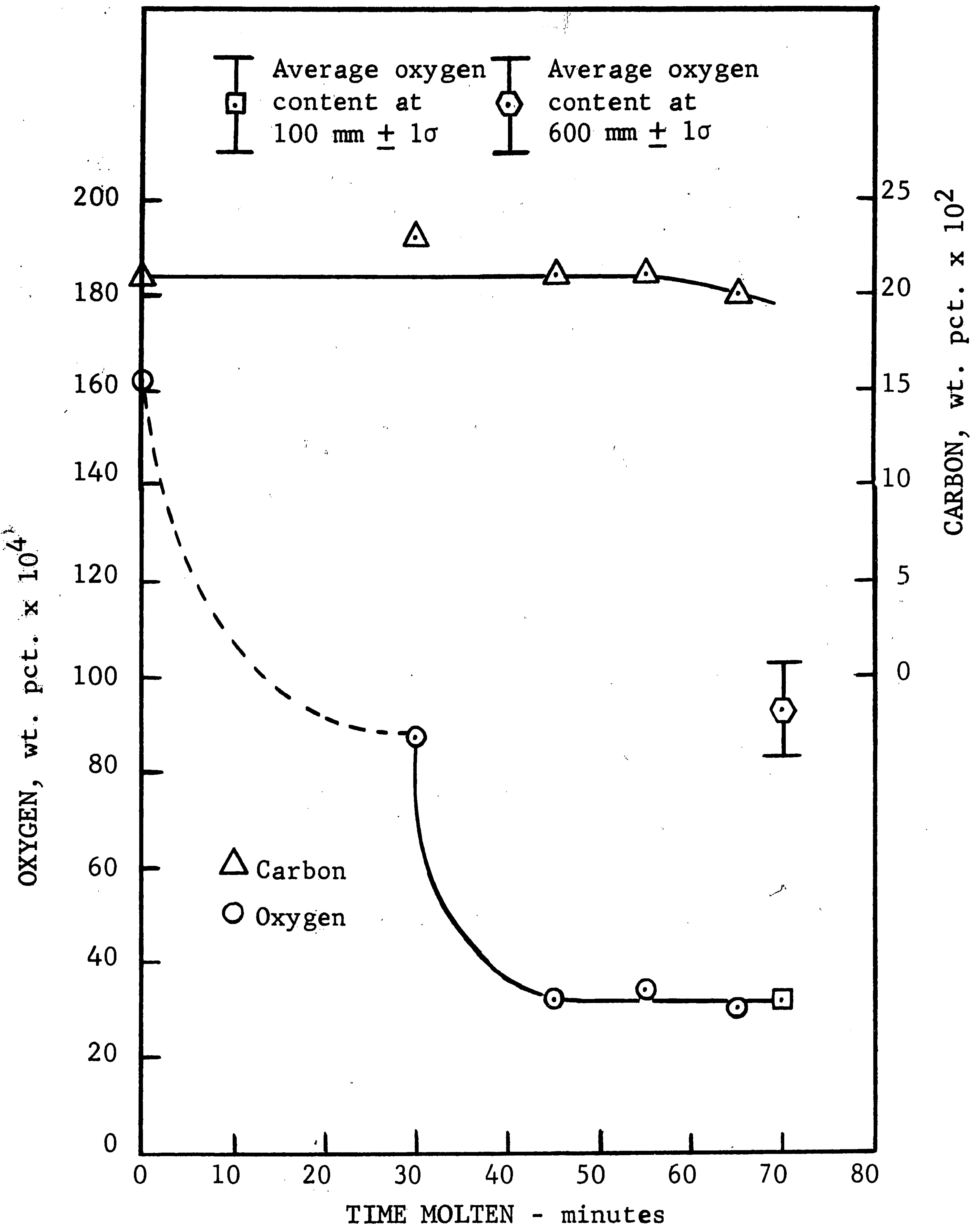

Figure 13 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 100 mm Hg. of CO (run 19).

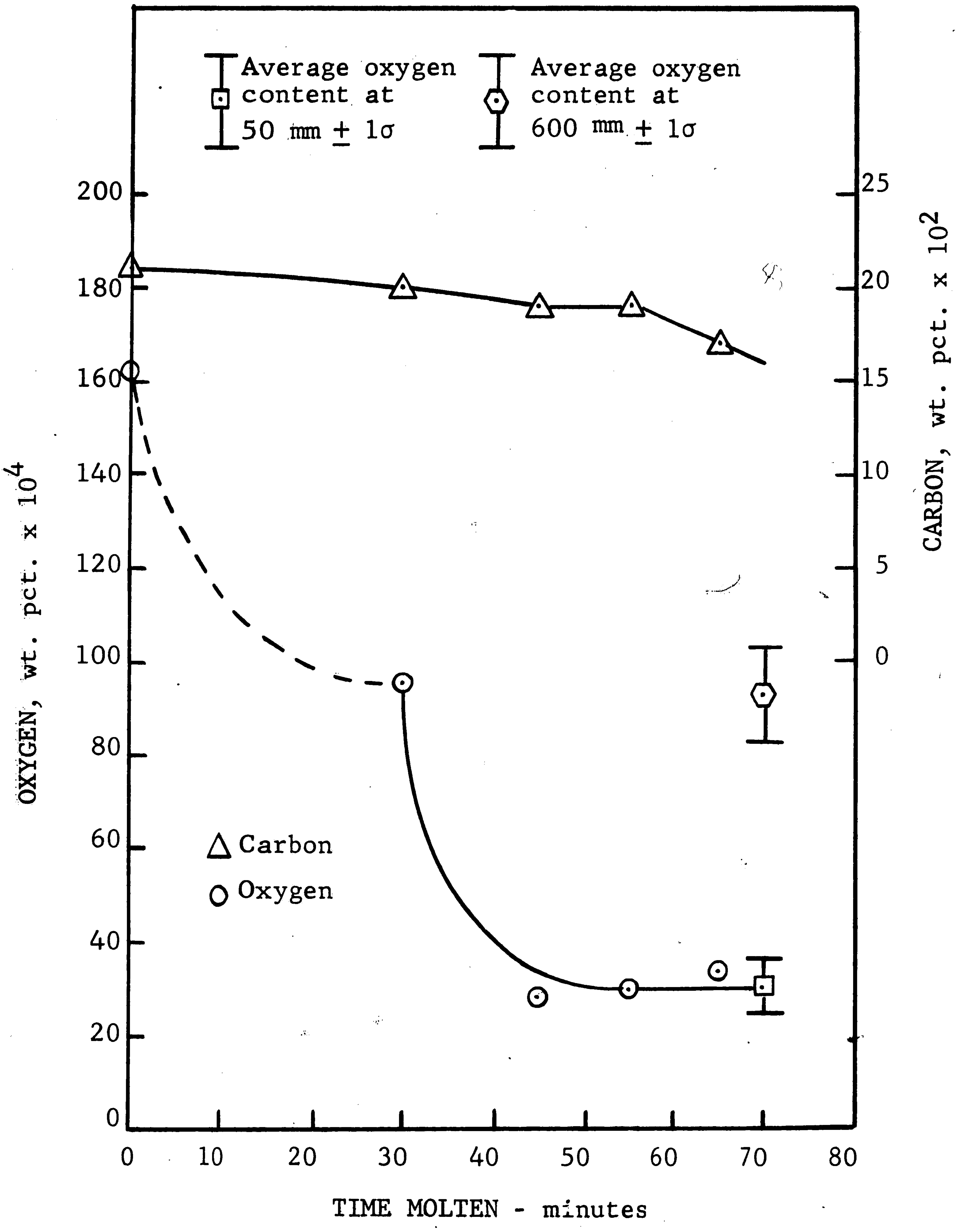

Figure 14 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 50 mm Hg. of CO (run 20).

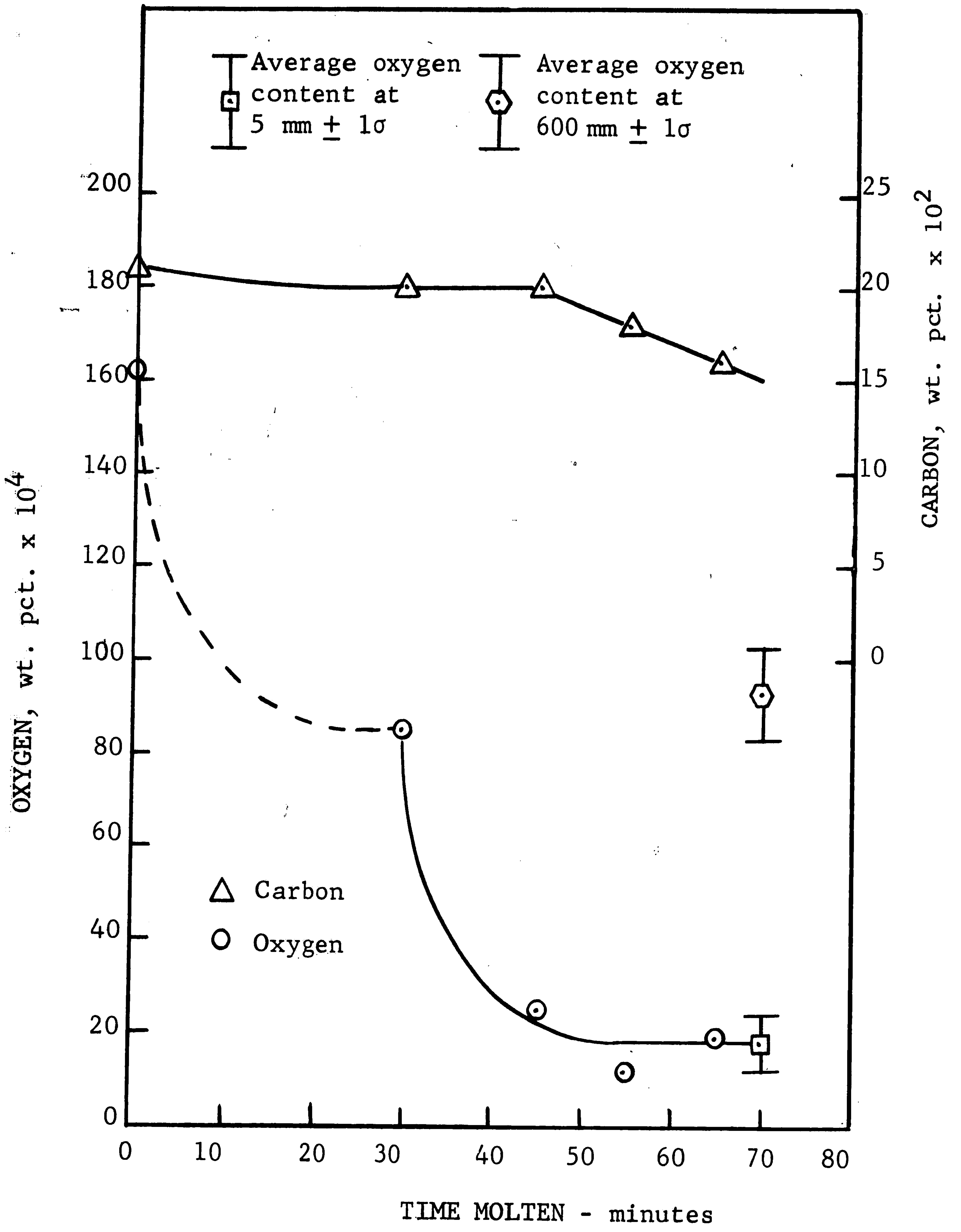

Figure 15 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 5 mm Hg. of CO (run 22).

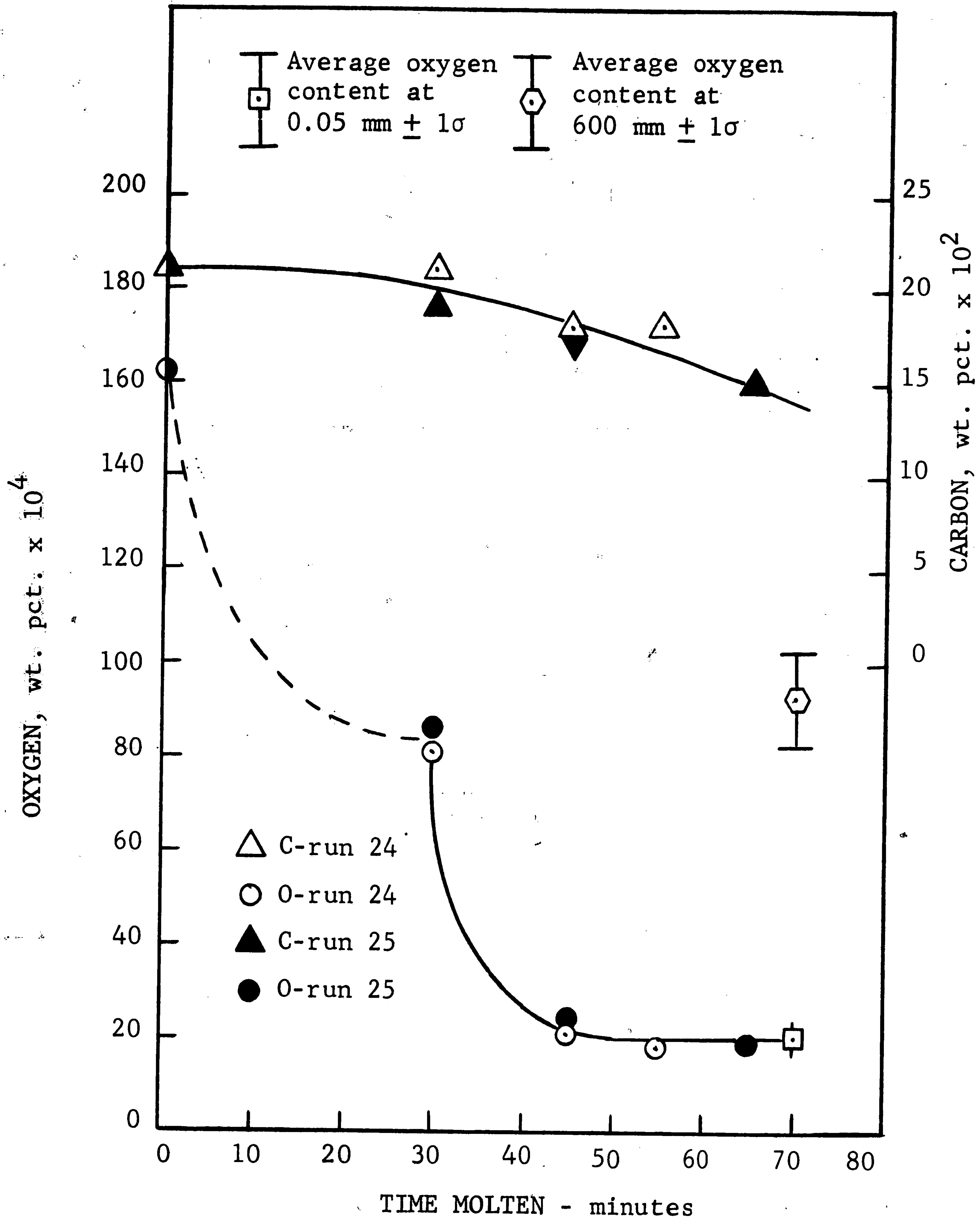

Figure 16 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 0.05 mm Hg. of CO (runs 24 and 25).

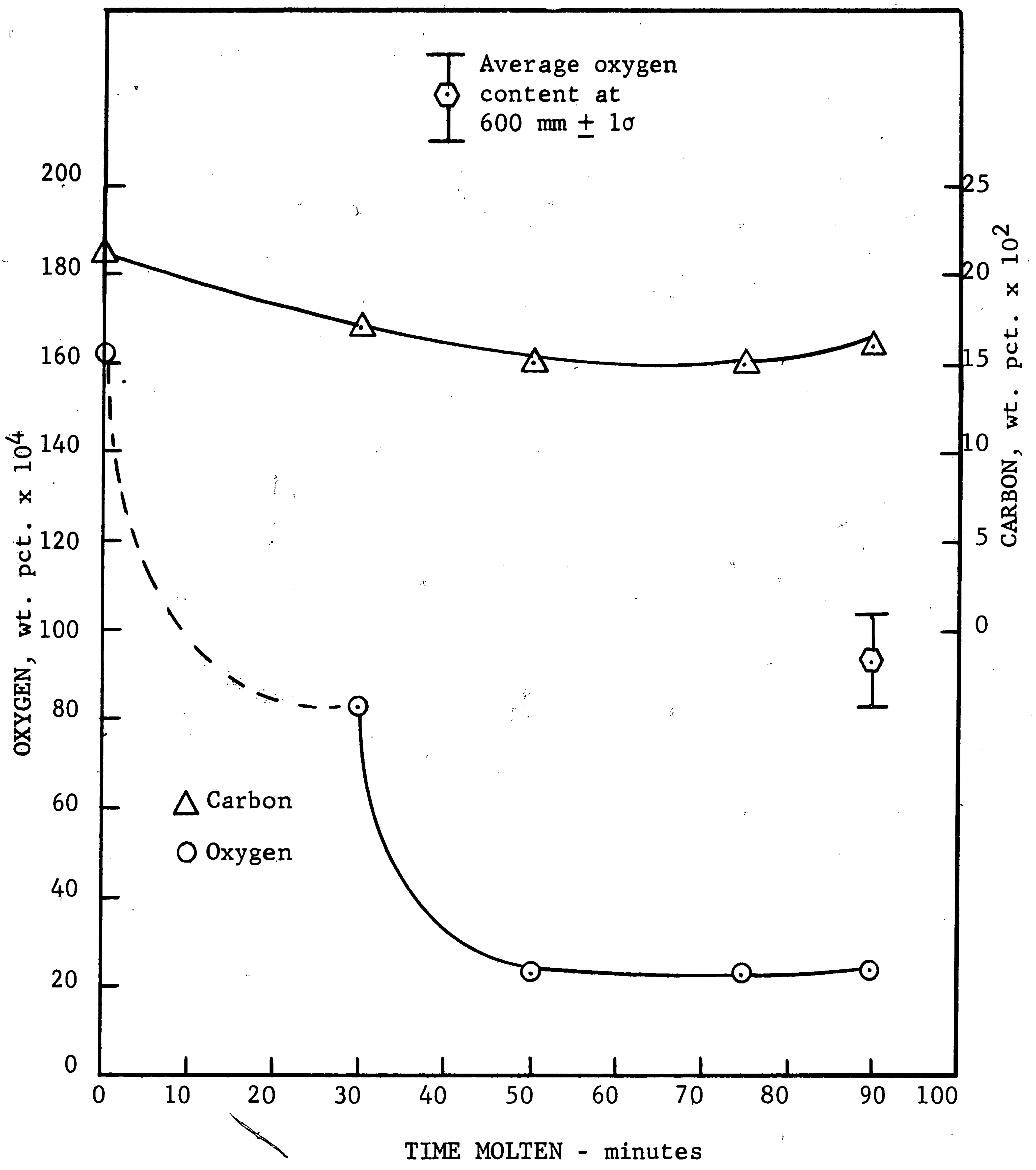

Figure 17 - Variations in carbon and oxygen content of an initially 0.21 wt. pct. C steel with time. Charge melted and equilibrated at 600 mm Hg. of CO. Bath treated at 20 mm Hg. of CO for 30 min. followed by 30 min. at 200 mm Hg. of CO.

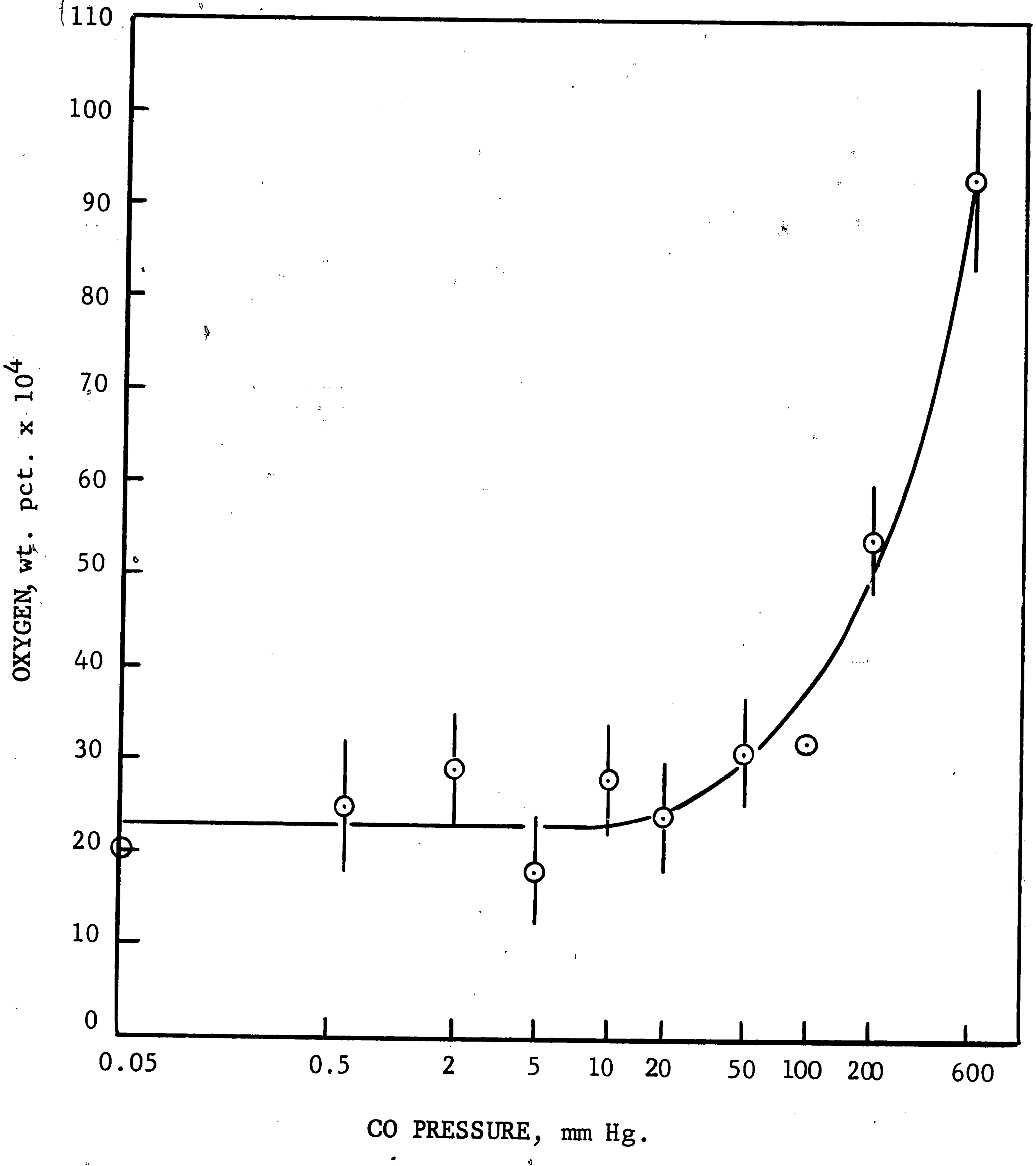

Figure 18 - Final oxygen content of initially 0.21 wt. pct. C steel melts as a function of the partial pressure of CO over the bath.

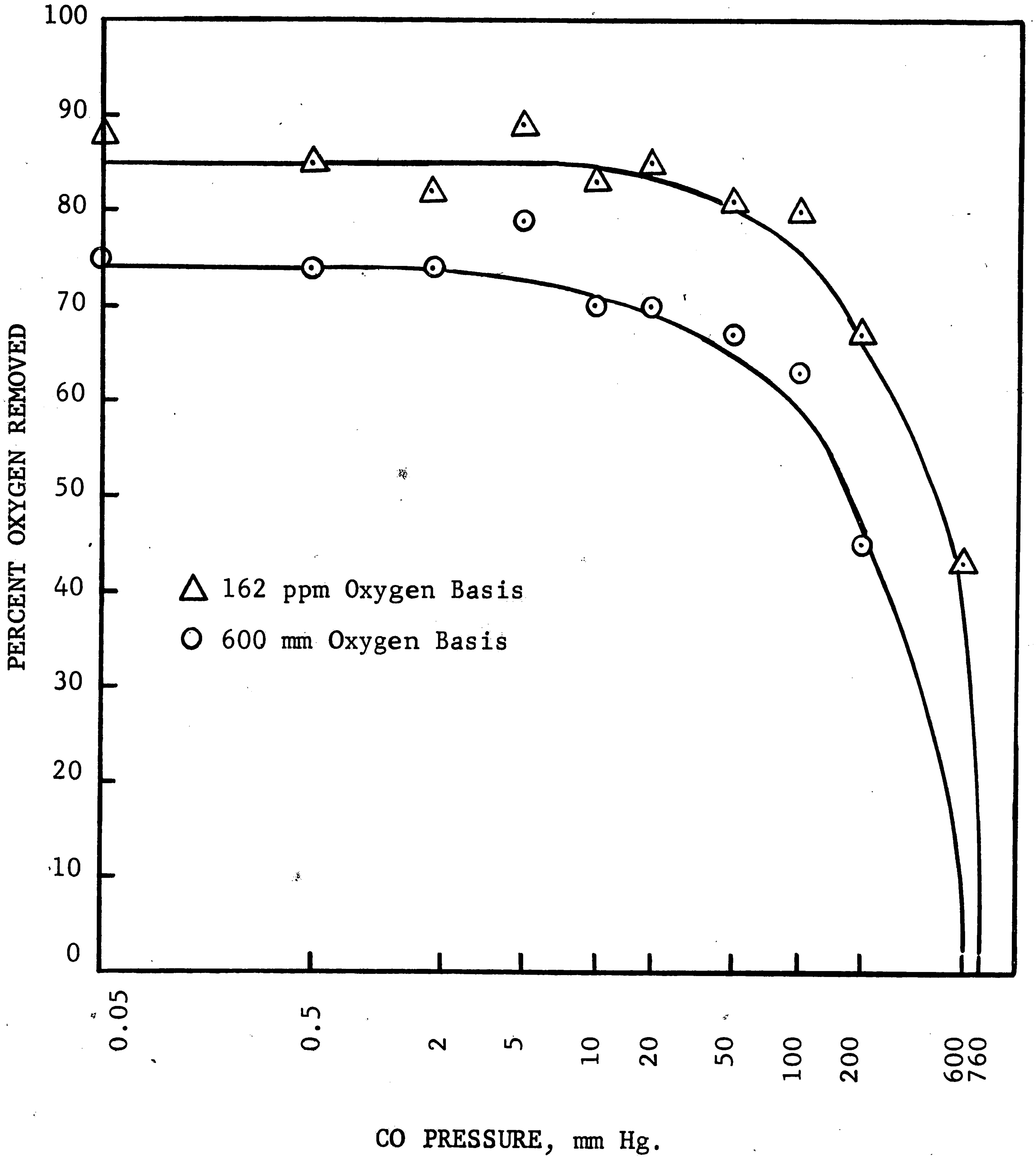

Figure 19 - Percent oxygen removed from initially 0.21 wt. pct. C steel melts as a function of the partial pressure of CO over the bath.

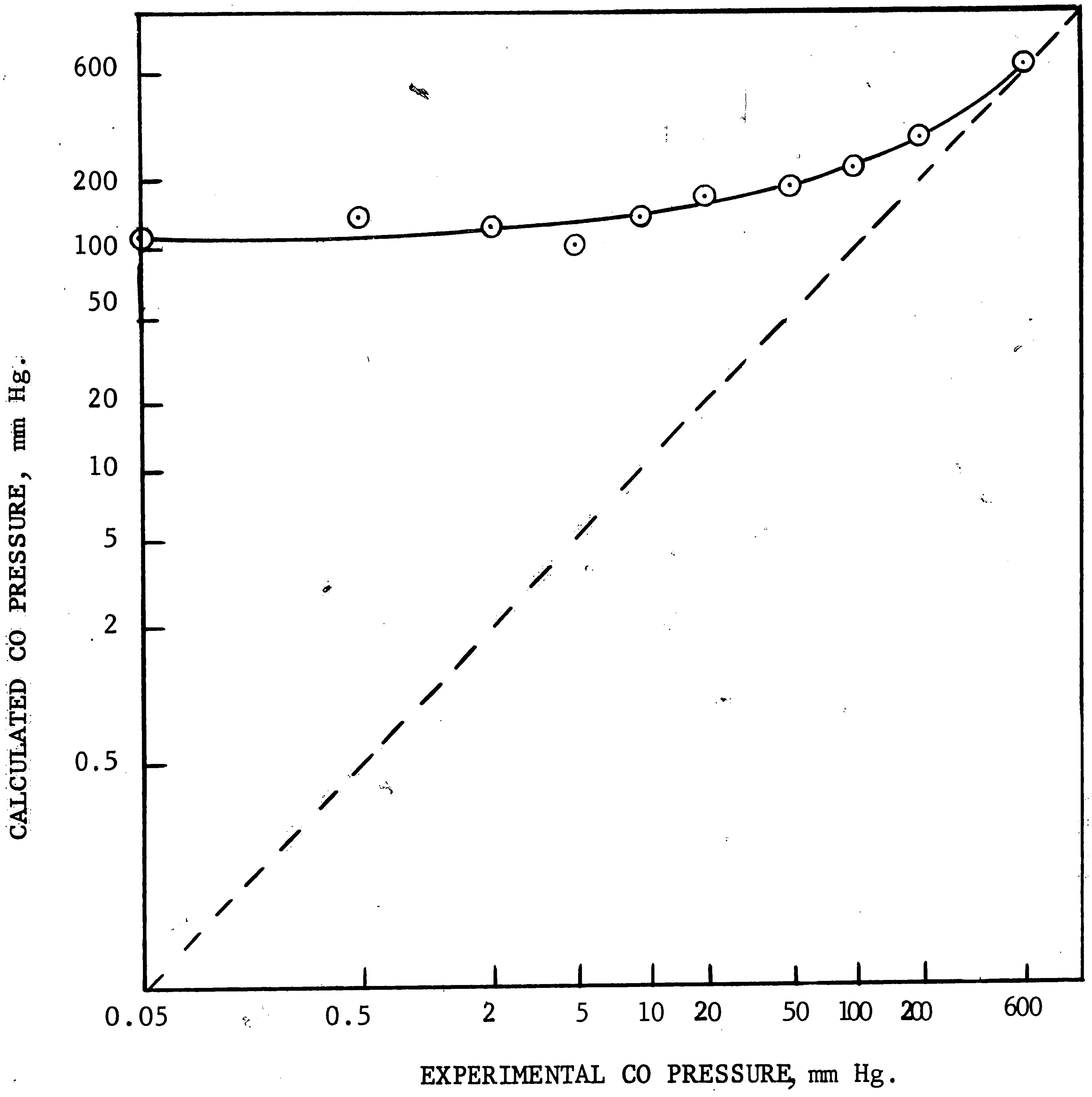

Figure 20 - A comparison of the calculated and experimental partial pressures of CO over initially 0.21 wt. pct. C steel baths.

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VITA

Arlan Edward Rathke, the son of Mrs. W. R. Rathke and the late W. R. Rathke of Hamilton, Montana, was born in Spokane, Washington, on September 29, 1936. He attended McKinley Elementary School in Butte, Montana and obtained his secondary education at Libby High School in Libby, Montana, where he graduated in June, 1954. The author entered the Montana College of Mineral Science and Technology at Butte, Montana, in the fall of 1954 and was awarded a bachelor of science degree in metallurgical engineering in June, 1958. Upon receipt of this degree the author was employed as a research and development trainee by the Inland Steel Company of East Chicago, Indiana. The following year he was promoted to a metallurgist in the steelmaking research section. In the fall of 1959, Arlan initiated graduate studies in engineering at the Calumet Campus of Purdue University on a part-time basis. In August of 1963, Arlan received an educational leave of absence and entered the Graduate School at Lehigh University as a research assistant on a project sponsored by the Bethlehem Steel Company.

Mr. Rathke is a member of Theta Tau and the American Society for Metals. In February of 1965 he was awarded United States Patent No. 3,169,857 "Improvement of Hot Workability of Free Machining Steels by Addition of Zirconium".

He is married and the father of four boys.