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I hereby recommend that the thesis prepared under my supervision by John F. Kahles

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Approved by:

Ray O. McDuffie

W. M. Burgess

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FORMATION AND TRANSFORMATION STUDIES
OF
IRON-CARBON POWDER ALLOYS

A dissertation submitted to the

Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

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1946

by

John F. Kahles
B.S. Illinois Institute of Technology

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

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In this work I have received generous assistance from many of my friends. I find it difficult to formulate a list that is short enough. I sincerely hope that my actions manifest at least in part how much I appreciate their efforts.

TO

B. W. K.

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INTRODUCTION

The ends achieved by the studies related in the pages that follow depend rather largely upon the viewpoint and interests of the person studying the results. In setting forth the problem of the study of reactions in iron-carbon powder alloys one of the prime interests was to determine whether reactions which occur in the solid state in ordinary steels are similar to those in the powder alloys. W. D. Jones (1) has pointed out that the powder approach to the solution of many intricate problems confronting metallurgists constituted a powerful tool. He states, "By the sintering method it is possible to vary the intercrystalline phase at will." Problems of grain growth, austenite decomposition, intergranular corrosion of stainless steels, season cracking in copper base alloys, carburization of iron, and graphitization of iron-carbon alloys are but a few of the many problems that may be approached from the powder state. By its methods one often has a better opportunity to incorporate constituents in a controlled fashion in solid solution and in additional phases that may lead to the analysis of a given problem. Of particular interest is the fundamental problem before metallurgists continually--namely, the nature of the grain boundary. Following are listed then the objectives sought in this study. Some of these developed as the research progressed:

I. How is the isothermal decomposition of austenite influenced when the steel is formed from the powder state?

II. How can steels be formed from the powder state and what factors are of particular import?

III. What are the carburizing characteristics of iron powder?

IV. What are the austenite formation characteristics of steels made from iron powder?

Some of the questions proposed are answered with some degree of satisfaction in this dissertation. The results, however, constitute but a small beginning toward thorough understanding of the objectives sought. One may say that new horizons are at least brought into view.

POWDER METALLURGY

In order to understand thoroughly the problems to be discussed some attention should be given to the general method used for the preparation of materials used in this study. Specimens were prepared by the methods of powder metallurgy practice. Powder parts in general are manufactured in relatively few and simple steps:

I. Formation of the powder

Many methods are available for the production of metal powders. They are:

A. Machining
B. Comminution
C. Shotting
D. Granulation
E. Atomization
F. Condensation
G. Precipitation
H. Electrodeposition from solutions including fused salt baths
I. Reduction of metal oxides
J. Distillation of a volatile constituent from an alloy
K. Carbonyl decomposition
L. Decomposition of metal hydrides
M. Intergranular corrosion

Of the methods listed reduction of metal oxides, electrodeposition, atomization, comminution, and carbonyl decomposition are at present most important commercially. In general, fine powders of varying mesh size that are not strain-hardened are desired. Certain applications, however, require coarse powders.

II. Pressing of the powder

The next operation requires pressing of the metal powder into parts of desired shape. This is often accomplished in the "cold state". That is pressing is done at ordinary temperatures with the pressures required varying over a fairly wide range, but in commercial practice being of the order of twenty-five tons per square inch. It is readily appreciated that the pressing pressures required tend to limit the size of parts produced by powder methods. In order to maintain low pressing pressures the powder is generally plastic so that many atomic bonds may be made in pressing. In some instances it is feasible to add graphite, stearic acid or other lubricants to the powder mix to facilitate formation of the part by lowering pressing pressures required. As the pressing pressure increases the density and hardness of the compact increase. Quite often high pressures are undesirable because gases which are present lower the density of the part during sintering. One significant point to recognize is that hydrostatic conditions are not maintained as pressing occurs. This leads to pressure gradients as compacting is accomplished with the result that, in sintering, one portion of the compact may even expand while another section contracts.

III. Sintering of the compact

While the compact formed by cold pressing may be handled conveniently, it does not possess generally sufficiently high mechanical properties to be of much value. It is essential therefore to heat the compact to elevated temperatures. In many instances this sintering temperature is well below the melting point or range of the alloy system considered. Sometimes one or more phases of the compact go into the liquid state. Before long, however, diffusion occurs and a solid is formed. In sintering, stress relief, recrystallization, and diffusion give rise to increased bonding. Some attention has been devoted to the temperature at which sintering begins. Without question the beginning of sintering occurs in the pressing of the powder, but not to a sufficient extent to give the required mechanical properties. For close dimensional control it is common to follow sintering by a sizing operation--a repressing in finishing dies to achieve set dimensional tolerances.

The "cold pressing" method is the one most widely used for production of powder parts, but there are several others of importance. The hot pressing practice accomplishes pressing and sintering simultaneously by use of hot dies. By this method one may produce higher density parts with lower pressing pressures. The maintenance of dies at elevated temperatures usually gives rise to much difficulty. Another method is one utilizing the cold pressing practice including sintering. These steps are then followed by a reheating and subsequent shaping by any of the conventional mechanical working procedures.

Through utilization of these methods for shaping parts from powders it has been possible to develop many interesting products:

I. Refractory metals

Since melting of the metal is not required it has been convenient to use the powder methods for production of such high melting metals as tungsten, tantalum, columbium, and molybdenum. These metals are difficult to melt and cast. Difficulties are encountered particularly in the selection of suitable refractories and in impurities, including gases, which are absorbed readily in the liquid state.

II. "Oil-less" bearings

These have been produced by the millions for varied applications. In electric shavers, sewing machines, phonographs, etc. many bearings are sealed into the units for the life of the machine. The oil required is introduced into the continuous pores that are developed by the cold pressing technique. Such continuous porosity, as high as forty per cent of the volume of the compact, cannot be achieved economically in cast metals.

III. Friction parts

Some very useful high temperature friction parts have been developed by the introduction of nonmetallic minerals in a metal base. Since it is difficult to disperse the lighter minerals properly in the liquid metal, powder methods are used.

IV. Dual Alloys

In an effort to achieve dual functions with certain alloys it was found necessary to make combinations such as copper-tungsten, silver-tungsten, etc. These combinations have excellent refractory characteristics along with good electrical conductivity. These dispersions are extremely difficult to develop satisfactorily from the liquid state.

The above are but a few of the many applications of powder methods where there is little or no competition from other methods of fabrication. In addition to these type applications are ones in which the powder method enters into competition with the more conventional procedures. In many applications, in spite of higher raw material cost, it is more economical to process powder rather than to form the product from the liquid state. It is this phase of powder metallurgy in which considerable interest has been shown recently. In fact this dissertation has direct bearing on the problem of powder metallurgy in competition with conventional fabrication procedures.

This section just concluded and titled "Powder Metallurgy" is intended to be but a brief sketch of the general procedures employed to aid the reader in the analysis of discussions to follow. References (1) - (11) inclusive are particularly valuable as sources of both general and specific information relating to problems in powder metallurgy.

THE POWDER METALLURGY OF STEEL

In recent years considerable interest has been shown in the field where powder metallurgy is competitive with other fabrication procedures. F. P. Peters (12) and A. J. Langhammer (13) in recent papers have discussed some of the questions relating to this general problem. Peters pointed out that from considerations of design powder metallurgy may be competitive with sand casting, die casting, permanent mold casting, precision investment casting, machined bar stock, screw machine parts, cold-heading, drop forging, stamping, and drawing. Langhammer discussed in a general way the advantages and limitations of powder metallurgy as applied to machine parts. In this field, from a material standpoint, much emphasis has been placed upon the use of iron and iron base alloys--in particular those alloys which are designated as steels.

Before and during World War II important applications were made of steels developed by powder methods, but it may be said that there is, as yet, not enough work of a fundamental nature in the literature. Some of the more interesting developments are summarized in paragraphs that follow.

W. D. Jones (1) has summarized the work of German investigators particularly E. K. Offermann, H. Buchholtz, and

E. H. Schulz. These men produced steels by sintering carbonyl iron powders of varying carbon and oxygen contents. To these powders they added graphite, ferromanganese, and other agents as desired. After sintering the ingots were forged into billets. Properties of these steels, including tensile strength, electrical resistance, magnetic properties, hardness, microstructural characteristics, heat treating properties, weldability, and others, were then studied and compared with steels produced from the molten condition. The results are quite detailed but one gets a very definite impression that the same condition of composition and grain structure in a steel may be achieved either from the liquid or solid state without too much difficulty. When one considers the subtleties possible in the condition of the grain boundary, this is a rather sweeping statement to make. Lest there be a misunderstanding it might be added that the equivalency referred to has not as yet been established but there is a distinct trend toward it.

C. W. Balke (14) has reported some of his studies on the effect of pressure on the properties of powder compacts. He made steels with electrolytic iron as a base and included carbon and other alloying elements necessary to approach steels designated ordinarily as S.A.E. 1000 series, S.A.E. 4560 and S.A.E. 3140. In the case of a certain manganese-molybdenum steel he found in certain respects the powder steel to be superior. Not enough information is given, however, to draw definite conclusions regarding equivalency.

J. Wulff (15) has reported on the production of a steel from powders which approached closely the composition of S.A.E. 4340. He too finds the properties of this material similar to those of the ordinary bar stock.

In addition to these attempts at producing powder alloys resembling the cast and wrought steels there have been a number of interesting developments where physical properties, though not approaching wrought steels, are more than adequate. F. V. Lenel (16) reported that a number of iron parts have been made and that some of these were used in quantities of a million or more. In particular he has interesting remarks to make concerning production of an oil pump gear used in automotive work. The microstructure developed might be considered more nearly that of cast-iron than of steel. The materials required for the production of the part are reduced iron and graphite. The resultant structure after sintering is graphite in a matrix of alpha ferrite and cementite. A large amount of the alpha ferrite and cementite are present in the microconstituent known as pearlite. Some of the advantages gained include: less raw material waste, more accurate contour resulting in better performance, porosity for oil impregnation, lower labor costs, and strengths equivalent to that of the cast iron gears formerly used. Some of the savings made in the production of powder machine parts have been astounding. In some British manufacturing procedures on gun parts 1,250,000 pounds of critical materials and 5,000,000 man hours were saved over a twelve month period during the recent war. According to Langhammer (13), even such parts as micrometer frames and V-blocks have been produced. The above publications along with countless patents in all countries have dealt with the problem of steel powder and parts production.

In reviewing the literature on steel parts from powders several general methods are prominent. Very frequently carbon in the form of graphite or carbon black has been introduced into the powder mix with hydrogen reduced or electrolytic iron. In some instances brittle alloys such as white cast iron have been pulverized and mixed in appropriate quantities into iron powders. In both methods satisfactory pressing and homogenization have been attained. One of the prime difficulties encountered in pressing steel powders into compact form is the poor plasticity which gives rise to poor green strength. The presence of an adequate quantity of the plastic iron powder obviates trouble to a marked degree. In some applications it has been sufficient to provide a soft layer on the surface of alloy powders. This may be achieved by a partial decarburization of the powder particles under conditions where no oxidation occurs. Alloying elements such as manganese, nickel, chromium and others have been introduced in the same way as carbon, (i.e.) by incorporating them in the powder mix. P. R. Kalischer in a discussion of work by Balke (14) states that by use of controlled atmospheres they have been able to maintain carbon contents in compacts to within 0.02-0.03 per cent. This is remarkable.

Another method to which there has been but brief reference in the literature is one involving carburization of a compact already formed. Carburizing and sintering may take place simultaneously--it might be termed carbasintering. Some work has been reported very recently by A. S. Margolies (17).

In reviewing the literature on production of steels from powders it is clearly evident that one of the important factors to consider is oxygen content of the metal powders, especially that in iron. In order to provide uniformity in the finished product negligible oxygen or at least uniform oxygen content is essential in powder production. Any number of so-called steel parts that have been examined microscopically are no more than iron base parts with iron oxide particles distributed in the matrix with little or no carbon present. An examination of many iron powders sold commercially reveals large quantities of iron oxide with no recognition made of quantities of oxide present.

In concluding one may say that the economy of lower strength iron base alloys, such as the oil-pump gear referred to earlier, is well established. There is, however, a trend toward the development of higher strength parts made of steel. These have every chance of meeting competition offered by other methods. At the same time the need for fundamental data on their formation, reactions, and performance is clearly manifest.

THE PRODUCTION OF STEEL COMPACTS BY CARBURIZATION

With the revealed interest in the development of high strength steels from powder, a logical study to make is one dealing with the heat treating characteristics of such steels. More specifically it would be valuable to have information concerning the austenite transformation characteristics of steel powder compacts so that they might be compared with the conventional materials. In starting this program it was decided to prepare as pure an iron-carbon alloy as feasible in order to maintain better control of the pertinent variables during the transformation of austenite.

The very first attempts at producing an iron carbon alloy to be used in this study were made by adding graphite to hydrogen reduced iron of relatively high purity. With the first experiments run, difficulty was encountered in getting carbon into the iron when the material was heated into the austenite field. Later it was found that this was caused by the high oxygen content of the iron powders and much more carbon than required for the alloy should have been added. Meanwhile thought was given to the possibility of carburizing pure iron compacts. Listed below are some of the typical analyses from which a selection was made.

Electrolytic Iron Powder - Annealed

Total Iron	99.50%
Copper	0.01
Silica	0.02
Manganese	0.027
Zinc	0.090
Nickel	None
Sulphur	0.001
Phosphorous	0.002
Free Carbon	0.005
Oxygen	-

Electrolytic Iron Powder

Metallic Iron	97.2%
Total Iron	98.0
Total Carbon	0.07
SiO_2	0.017

Hydrogen Reduced Iron Powder

Total Iron	99%
Carbon	0.04
Manganese	0.18

Carbonyl Irons

Grade	% Carbon	% Oxygen	% Nitrogen
L	0.005-0.03	0.1 -0.2	0.005-0.05
C	0.03 -0.12	0.1 -0.3	0.01 -0.1
E	0.65 -0.80	0.45-0.60	0.6 -0.7
TH	0.5 -0.6	0.5 -0.7	0.5 -0.6
SF	0.5 -0.6	0.7 -0.3	0.5 -0.6

The statement carried along with the above analyses is "With reference to the chemical analysis shown above it should be noted that spectroscopic analysis shows the rest to be iron with other elements present in traces only." Inasmuch as chemical purity was a requirement for this study, it was very easy to make a choice of material. The logical choice was Carbonyl-L. By carburizing this iron in compact form it was possible to produce uniform composition samples that could be used for austenite transformation studies. In a very general way the following procedure was adopted.

I The carbonyl iron "L" as received from the manufacturer was subjected to a hydrogen drying treatment at low temperatures.

II The iron as prepared in step I was pressed into compact form in a steel die.

III These samples were then weighed on an assay balance to 0.01 of a milligram.

IV The weighed samples were then packed in hardwood charcoal. The carburizing time and temperature were controlled to obtain the desired carbon analysis in the specimens.

V The specimens were weighed in order to determine the weight increase.

VI The specimens were homogenized in a nitrogen atmosphere at elevated temperatures and reweighed after this treatment.

VII While carbon contents were determined by the weight increase, actual chemical analyses were made by several laboratories to compare the methods so that a correlation could be made.

The samples as prepared above were then cut into smaller pieces for the studies reported in the following section of this dissertation. Before developing this phase of the work consideration is to be given to some of the details of the steps just mentioned and to some of the results achieved.

I

The carbonyl iron "L" was treated with dry hydrogen at a temperature of 260°C for twenty-four hours. The hydrogen was bubbled through a mass of powder kept in a vertical position. The gas seemed to make good contact with the powder particles. After treatment there was a noticeable improvement in the color and chemical activity of the powder. One might consider that the treatment given would lead to a highly reactive surface that might pick up even larger amounts of oxygen. As will be shown later this is not the case for the chemical analyses compared with the weight changes in carburizing indicate a lower oxygen content than the 0.1-0.2% reported for this powder.

The temperature of 260°C was chosen because it was possible to keep the powder from going into lumps at this temperature. If lumps formed they could be disintegrated by shaking the tube in which the powder was treated. At temperatures around 285°C considerable lumping occurs--in fact in some runs all of the powder was in a fairly hard mass. The only information available from the manufacturer is that sintering occurs below 500°C. From work on carbonyl "L" and "C" it would seem to occur around 285°C in a hydrogen atmosphere. Some work on carbonyl "C" showed that there was no color improvement, (ie) brightening of the powder, when it was treated as above for eighteen hours at 150°C.

When the reduced powder was tested with concentrated nitric acid it was very reactive. With many of the fine iron powders it is possible to add the nitric acid without having any reaction apparent. In some cases a very slow addition, a drop running down the side of a test tube, will give rise to a vigorous reaction. In the freshly prepared irons above it was impossible to add the nitric acid fast enough to prevent reaction; it was almost explosive in character.

Some passivity tests were also run on the powder using a copper nitrate solution. Directly after reduction with hydrogen the reaction as noted by a color shift in the solution from blue to green takes place rapidly. In one test with freshly reduced powder it took but two minutes to show a shift while after forty minutes it took six and one-half minutes. Four days later it took twenty minutes. The carbonyl "L" without hydrogen treatment showed a time of approximately twenty minutes also. If the test is carried to a point where the solution is quite definitely green, the reduced powders generally take more time. Not enough tests were run to gain knowledge of any appreciable significance.

By drying the powder and eliminating some of the oxygen it was possible to obtain a powder suitable for making carbon analyses by weight changes.

II

The compacts used were pressed in a small heat-treated high carbon, high chromium steel die. Care was taken in the design of the die to provide uniform loading. Press capacity was limited so a Brinell hardness tester was used to supply the load. The dimensions of the compacts were 1/4" in diameter and thickness of the order of 0.035". They weighed of the order of 0.2 grams. They were kept small to minimize pressure variations through the compact. The load used for the samples was 3000 kg. Considering the exact dimensions of the sample the pressing pressure used was 138,000 psi. This was sufficient to give dense enough samples so that no difficulty was encountered in preparation and subsequent microscopic examination.

III

After careful brushing of the samples they were weighed on the assay balance as indicated previously. In no case were the compacts handled except with tweezers used ordinarily for analytical weights.

IV

Forty specimens as prepared above were then transferred to a 3/4" capped short pipe nipple. The nipple was filled with a 200 through 150 mesh hardwood charcoal surrounding the samples. This capped nipple was then placed inside of a similar but larger nipple, a 1 1/2" size. Similar charcoal was also placed in the larger nipple. This tube-within-a-tube combination circumvents any difficulty of samples staining by drawing air in upon them during cooling. More consistent carbon pick-up was also obtained by this practice as compared with single tube practice. These samples were carburized for fifteen hours at 870°C under carefully controlled temperature conditions. The sample weights in the lot of forty varied from 0.13721 to 0.22694 grams. This combined with packing variations and the fact that the nipple was "overcrowded" gave rise to more than usual variation in the weight gains. The variation was from 0.35% to 0.91%. There were enough samples of the same content to carry out the necessary tests. For example twelve of them were in the range 0.85-0.86%, fourteen in the range 0.87-0.88% and nine in the range 0.90-0.91%.

Whenever tests were run with fewer samples, after the technique was acquired, much better results were secured. Typical are the following, not necessarily carburized at the temperatures and times used for the larger batch.

A.	5 samples	0.88-0.89%	weight increase
B.	5 samples	0.71-0.72%	weight increase
C.	5 samples	0.61-0.64%	weight increase
D.	6 samples	0.84-0.85%	weight increase
E.	4 samples	0.97-0.99%	weight increase
F.	2 samples	0.72%	weight increase
G.	2 samples	0.78-0.79%	weight increase
H.	2 samples	0.52%	weight increase

These results show that check results are attained, and without too much difficulty it might be added.

V

In order to make the weight analyses indicated previously the samples were carefully removed from the carburizing pack and then brushed to remove any of the carbon dust that might have adhered to them. The samples as carburized are perfectly bright.

VI

After weighing, the samples used for further work were homogenized in a nitrogen atmosphere for three hours at a temperature of 1105°C. After removal from this atmosphere the samples were reweighed. Tests with samples of wrought steels in the nitrogen atmosphere used show extremely small changes in weight. Typical would be a loss of 0.00001 g in a sample weighing 0.36519 g in a period of twelve hours at 1095°C. The same sample showed no change in weight in 2 1/2 hours at 1040°C. The sample was carefully handled for the tests and weights used were left undisturbed on the balance pan.

The train developed mainly by E. E. Stansbury (18) is described in detail by him. It consists of the following items through which tank nitrogen of high purity is passed.

A. A tower of soda-lime

B. Two bubble towers of concentrated sulphuric acid

C. Tube of freshly reduced copper maintained at about 300°C

D. A long tube of magnesium perchlorate at room temperature

E. Steel wool just ahead of the sample in the silica tube in which the homogenization is accomplished.

The silica tube is equipped with a solenoid so that samples may be flushed by the furnace atmosphere and may also be allowed to cool in the colder portion of the tube in the same nitrogen atmosphere. The train is regenerated as required with tank hydrogen.

VII

For one set of tests on carburization several larger compacts weighing between two and three grams were prepared in a 3/8" diameter die. These samples were carburized and the weight gains noted. They were then run for carbon by the usual combustion method. Results were:

Weight % gain	Chemical Analysis % Carbon
1.17%	1.21%
1.13	1.20
1.13	1.17
0.76	0.83

In addition a set of six of the forty compacts averaging 0.88% weight pickup showed a value of 0.95% carbon. Another set of six samples of the same group were checked after being homogenized at 1105°C. The weight percentage was 0.91% (based upon weight after carburizing) while the carbon determination gave 0.93% C. Other results on single samples weighing about 0.2 g and after homogenization show comparisons that are consistent.

Weight %	Carbon %
0.72	0.74
0.89	0.93

During homogenization there is always a weight loss on the compacts. This is because oxygen that is present after the carburizing cycle combines with carbon to go off in the form ($CO-CO_2$). The train was always checked carefully to see that it was not the N_2 atmosphere causing this loss. Some conception of the loss may be gained from the following table:

	Original Weight as Pressed (g)	Weight after Carburization (g)	Weight after Homogenization (g)
A.	0.18740	0.18902	0.18894
B.	0.20071	0.20242	0.20234
C.	0.20387	0.20564	0.20554
D.	0.20788	0.20973	0.20964
E.	0.17659	0.17811	0.17802

It would appear that by making the appropriate correction the carbon analysis of any sample could be ascertained from a carefully made weight gain check.

Spectrographic estimates were conducted on samples in various stages of processing.

A. Carbonyl iron "L" as received.

The following elements were checked but not found: copper, silicon, sodium, manganese, nickel, chromium, cobalt, molybdenum, vanadium, tungsten, lead, tin, antimony, aluminum, titanium, zinc, calcium, barium, and strontium.

B. Carbonyl iron "L" after the hydrogen treatment and pressing only

Same as in A.

C. Carbonyl iron "L" after carburization

Same as in A but two out of three samples showed an estimated quantity of copper equal to 0.0001-0.0009%.

D. Carbonyl iron "L" after carburization and then with homogenization at 1105°C

In addition to 0.0001-0.0009% copper it revealed an estimated 0.0001-0.0009% of silicon. Otherwise the sample was like A.

The compacts thus prepared can logically be considered to be relatively high purity iron-carbon alloys of known carbon content. Those selected for transformation studies had an actual carbon content computed to range from 0.87-0.89%C and a density after homogenization of 7.2 g/cc.

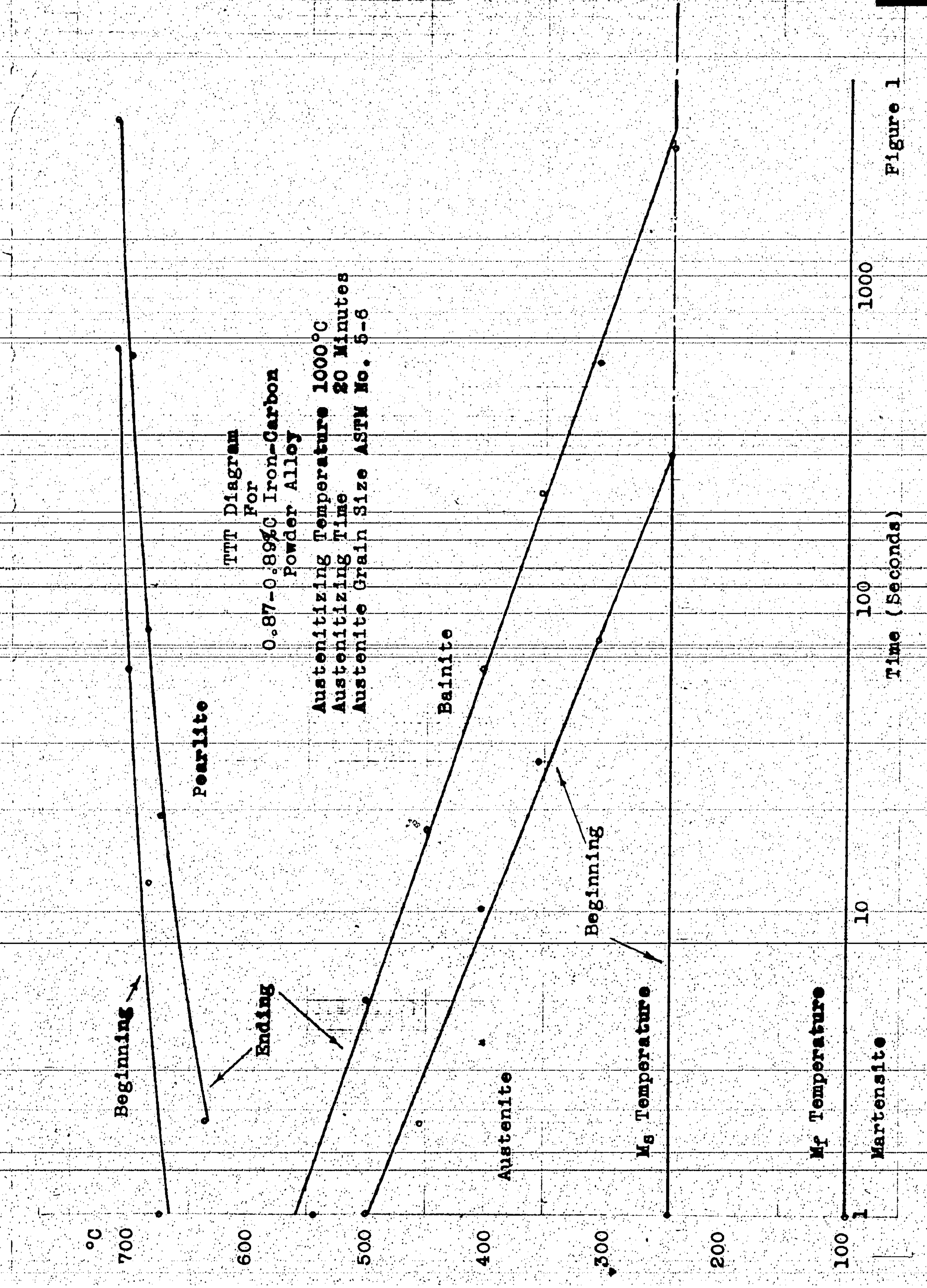
AUSTENITE DECOMPOSITION STUDIES ON IRON-CARBON POWDER COMPACTS

The steels made from powdered iron by carburization were studied further to determine their austenite transformation characteristics. As indicated previously the carbon content of the steel selected for this work was 0.87-0.89%C. The TTT (time-temperature-transformation) diagram or "S" curve for this steel is shown in Figure 1 and the data from which the curve is plotted are listed in Table I. The conditions under which the data were obtained are as follows:

I Austenitizing was accomplished at a temperature of 1000°C for twenty minutes in the same nitrogen atmosphere used for homogenization of the samples after they had been carburized.

II Small notched samples (dimensions approximately 0.035" square and 1/8" long) were suspended in the atmosphere by a small stainless steel wire (0.003") attached to a nickel wire (0.066"). The small samples were made by cutting the 1/4" diameter compacts into seven or eight pieces with a jeweler's saw. The structure is shown in Figure 3.

III The samples were held in the nitrogen atmosphere in the cold portion of the tube for flushing. They were then advanced into the hot zone of the furnace.



TTT Diagram
For
0.87-0.89%C Iron-Carbon
Powder Alloy

Austenitizing Temperature 1000°C
Austenitizing Time 20 Minutes
Austenite Grain Size ASTM No. 5-6

Figure 1

S-Curve for 0.89% Carbon Steel

(*Transformation of austenite at constant sub-critical temperature*)

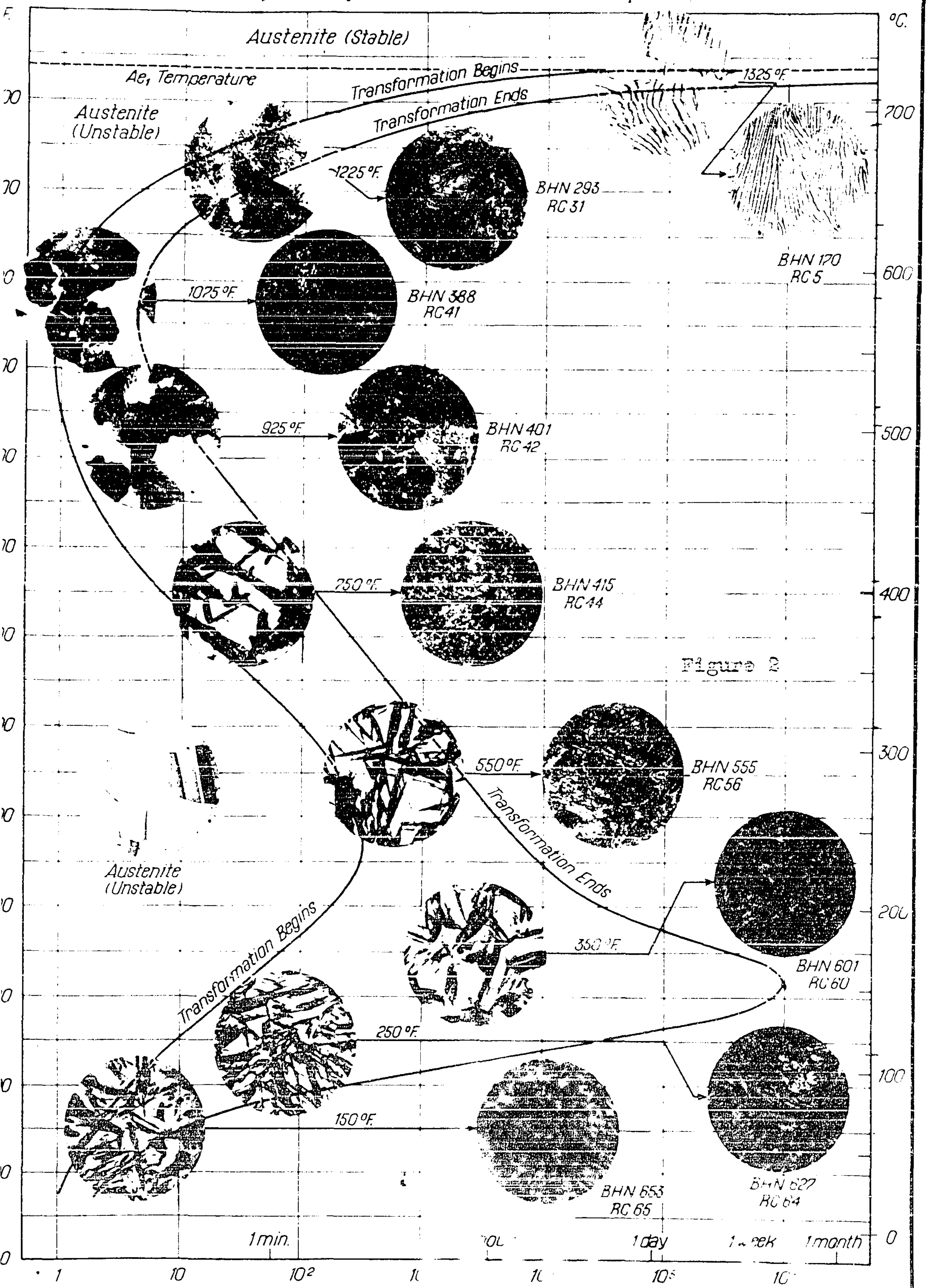


Figure 2

Courtesy, U. S. Steel Corp. Research Laboratory

Metal Progress

Table I

Data for TTT Diagram in Figure 1

Sample No.	Temperature (°C)	Time (Seconds) Beginning	Time (Seconds) Ending
	Pearlite Formation		
I98	714	660	
I100	713		>3000
I34	704	60	
I36	704		630
I83	688	12	
I84	688		80
I9	676	1	
I5	676		20
-	639	?	
I63	639		2
	Bainite Formation		
-	546	?	
I62	546		1 or less
I59	500	1	
I60	500		5
I57	455	2	
I68	450		18
I46	404	10	
I53	404		60
I65	353	30	
I70	353		225
I61	308	75	
I64	308		600
I77	244	300	
I78	244		3000

Martensite Formation

M_s Point 242°C

M_f Point 96°C

In order to support the nickel wire the end was inserted into the rubber stopper which was used to close the silica tube. After holding for twenty minutes at 1000°C, the samples were quickly transferred to the metal baths.

IV Lead was used as a quenching medium in the upper temperature ranges and the quaternary eutectic (Bi 50%, Cd 10%, Pb 27%, Sn 13%) was used for work at lower temperatures. For determination of transformation characteristics to pearlite or bainite the samples were quenched in a dilute NaOH solution directly from the metal baths. When martensite studies were conducted, the samples were tempered at 280°C for 10 secs. prior to quenching in the dilute NaOH solution.

V The analyses of the transformation products were all made by microscopic examination. Figures 4 to 33 show the typical structures that were obtained in developing the TTT diagram (Figure 1).

There are a number of comments of interest that may be made with respect to this diagram. First, it may be stated that it is subject to the limitations of the metallographic method of analysis. It is very difficult to decide when a product first appears and when transformation to it has been completed. This is to be expected when one considers the kinetics of austenite decomposition. In the diagram shown this work was done carefully but not scrupulously. In the opinion of the author the diagram represents an excellent estimate of the transformation of austenite. A conservative estimate would be a 10% variation in placing beginning and ending times except at temperatures where very rapid transformation occurs.

It is interesting to note that the reactions are not far different from TTT diagrams for wrought steels. A comparison is difficult to make for no one has published, as far as I know, a TTT diagram for a high purity wrought iron alloy. However, one diagram exists for a 0.89% carbon steel with 0.3% manganese (Figure 2). No other elements have been reported but it is believed that small quantities of silicon, sulphur, and phosphorus at least are present.

The lower region where martensite formation occurs is entirely wrong in Figure (2). However, it was possible to compare the M_s points for the powder and wrought alloys. A. B. Greninger (19) showed an M_s point for a 0.85%C iron-carbon alloy of about 240°C. The data in Table I shows an M_s point of 242°C for the steel considered. It would appear that these are no different from similar points found in wrought pure steels. In other words the fact that the density of the powder compact is but 7.2 g/cc as compared to 7.80 g/cc for the wrought pure steels makes no difference in the beginning and ending of martensite formation. Whether this is true for a less dense compact has not been ascertained. Further it is not known whether the rates of martensite formation with temperature drop are the same. In other words while the M_s and M_f points are the same the transformation characteristics could deviate within this range.

It is of interest to note that in the upper part of Figure 1, there is a large range where very rapid reactions occur. Just what the transformation characteristics are in this range has not been determined. They must certainly be extremely rapid for such high purity alloys as used in these experiments.

Both pearlite and bainite beginning and ending lines seem to be fairly straight when plotted on semi-log paper. An examination of the curve as drawn would lead one to believe that the most rapid rate of transformation is somewhere between 600 and 650°C instead of around 550°C as shown in the diagrams of eutectoid plain carbon steels published previously by other investigators. Some theoretical deductions by C. Zener (20) indicate that the nose of the TTT diagram should be higher than 550°C.

A remaining item of particular interest (not shown in Figure 1 but for which microstructures are shown, Figures 11, 12, 13) is the rapid rate at which spheroidization occurs. This is no doubt a function of the purity of the alloy rather than the fact that the material is a powder compact. For example at 688°C spheroidization was noticeable in 15 minutes and almost complete in 93 minutes . In controlling physical properties in relatively high purity alloys in isothermal transformations it would be essential to know when spheroidization occurs after formation of the pearlite.

In addition to the TTT diagram determined some points were compared with a variation in the austenitizing temperature. Scattered studies were made with austenitizing temperatures varying from 875°C to 1100°C and with transformations to pearlite, bainite, and martensite. There was little variation if any from the results shown at 1000°C. This may be attributed to the fact that there were no marked changes in grain size for the times and temperatures used. More detailed studies are necessary to be certain of the results.

PHOTOMICROGRAPHS

Figures 4-33 inclusive are photomicrographs taken of the transformation products of austenite decomposition for the 0.87-0.89% C "powder" steel. They were all taken at 1000 diameters magnification with a 54X oil immersion objective. Etching was done with a solution containing 100 cc absolute alcohol, 2 cc of fuming nitric acid and 0.5 g of urea.

Other photomicrographs in this dissertation were also etched in a similar manner and photographed at 1000 diameters.

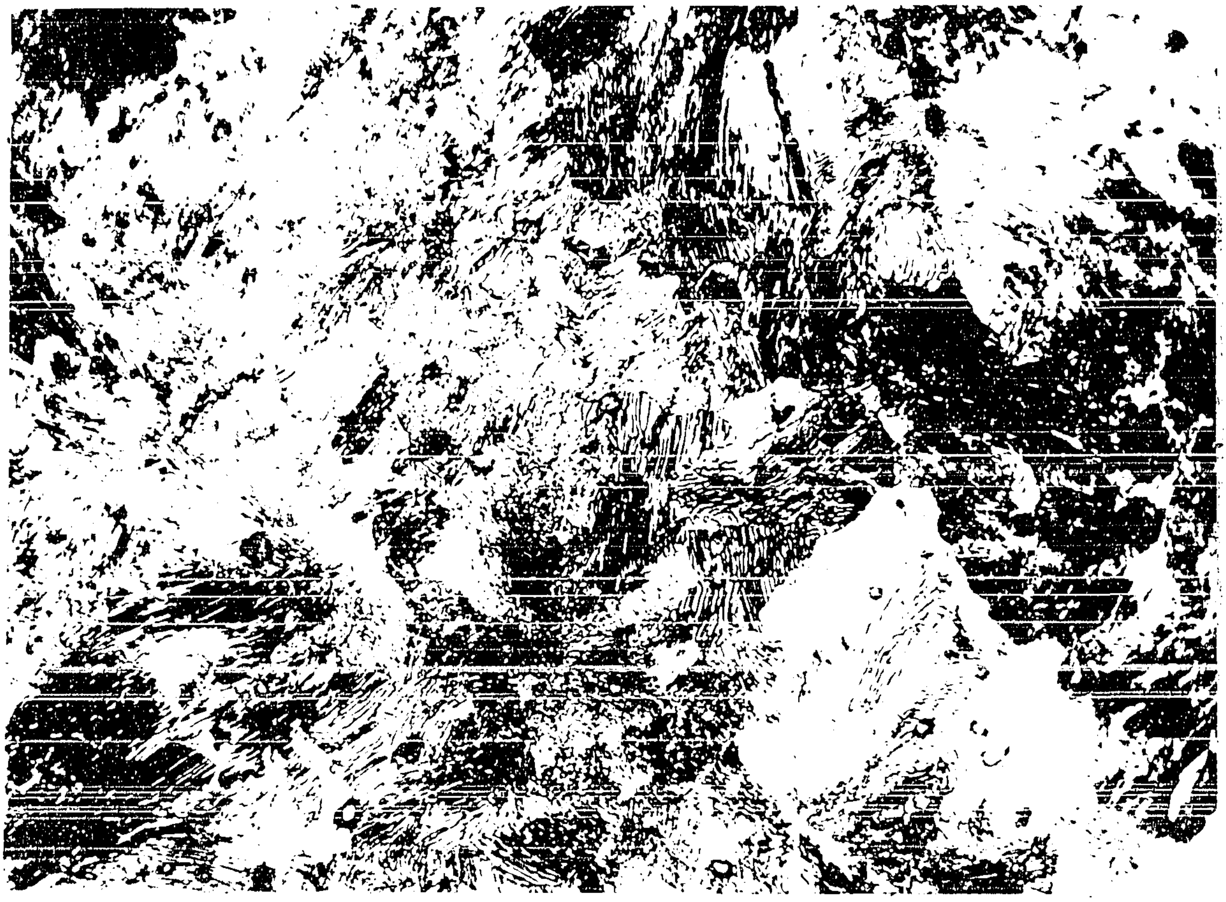


Figure 3
Sample No. 138

Fine pearlite, the structure of the 0.87-0.89% C steel following homogenization. In this form it was used for the isothermal transformation studies.

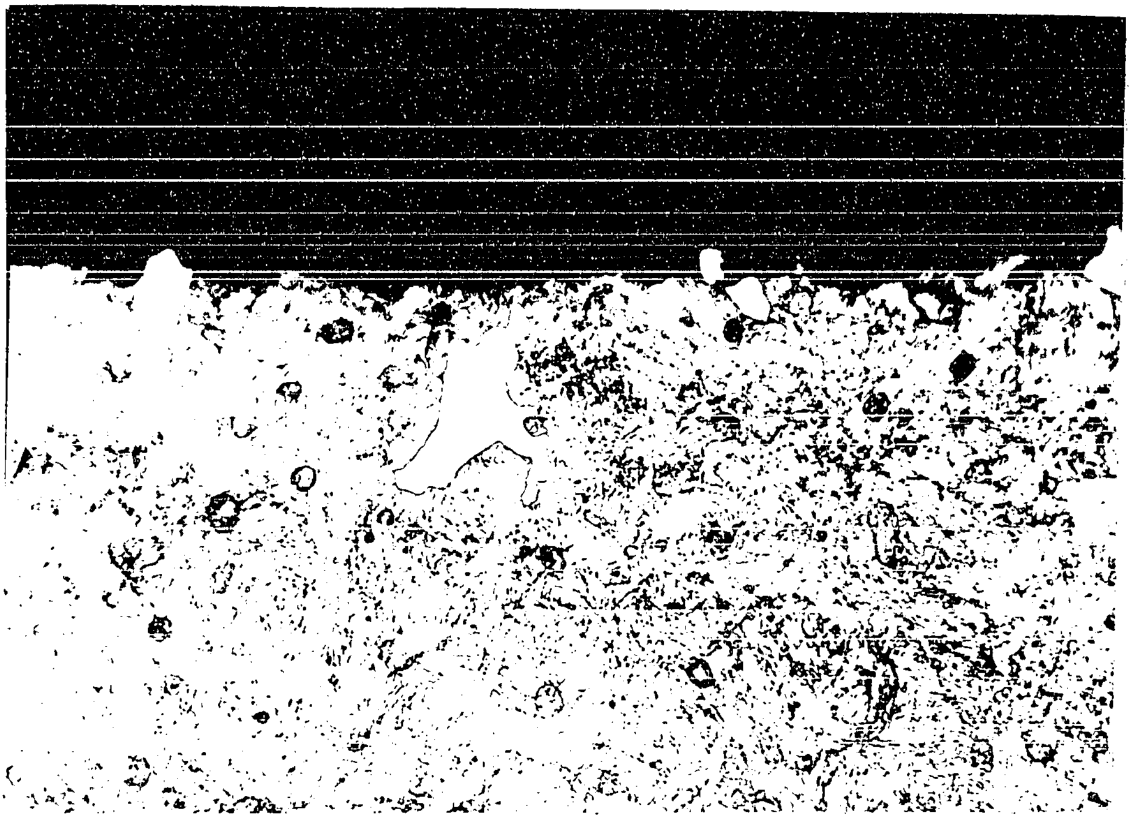


Figure 4
Sample No. I103
Isothermal transformation temperature 720°C
Time 60 minutes

Cementite and Martensite

Cementite is beginning to form near the edge of the sample. No transformation was shown in the center of the specimen. In this and in all other photographs of isothermal transformations the martensite is equivalent to austenite untransformed at the isothermal transformation temperature.

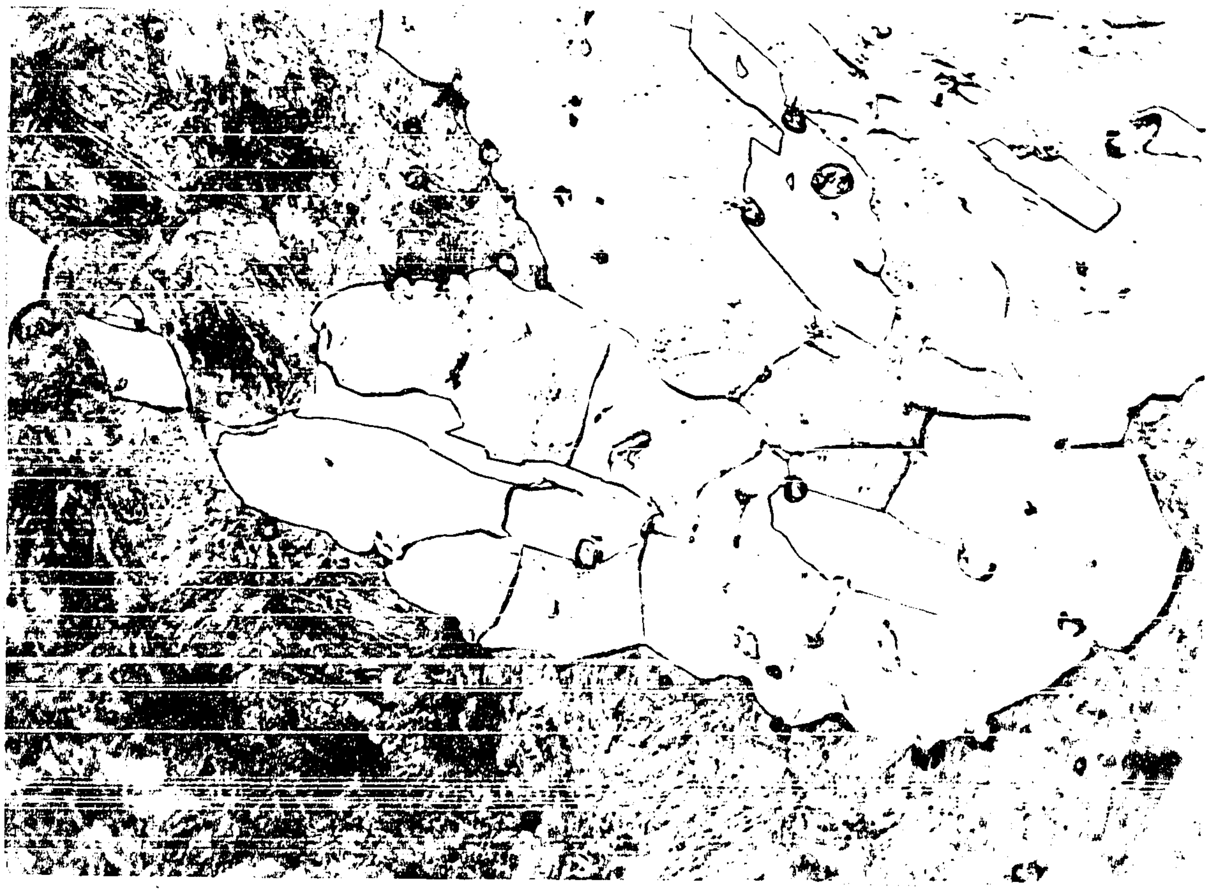


Figure 5
Isothermal transformation temperature 720°C
Time 15 1/2 hours

Alpha Ferrite, Cementite, and Martensite

Large crystals of cementite are shown. This sample was not used in plotting data for Figure 1. The austenitizing temperature was 1050°C.

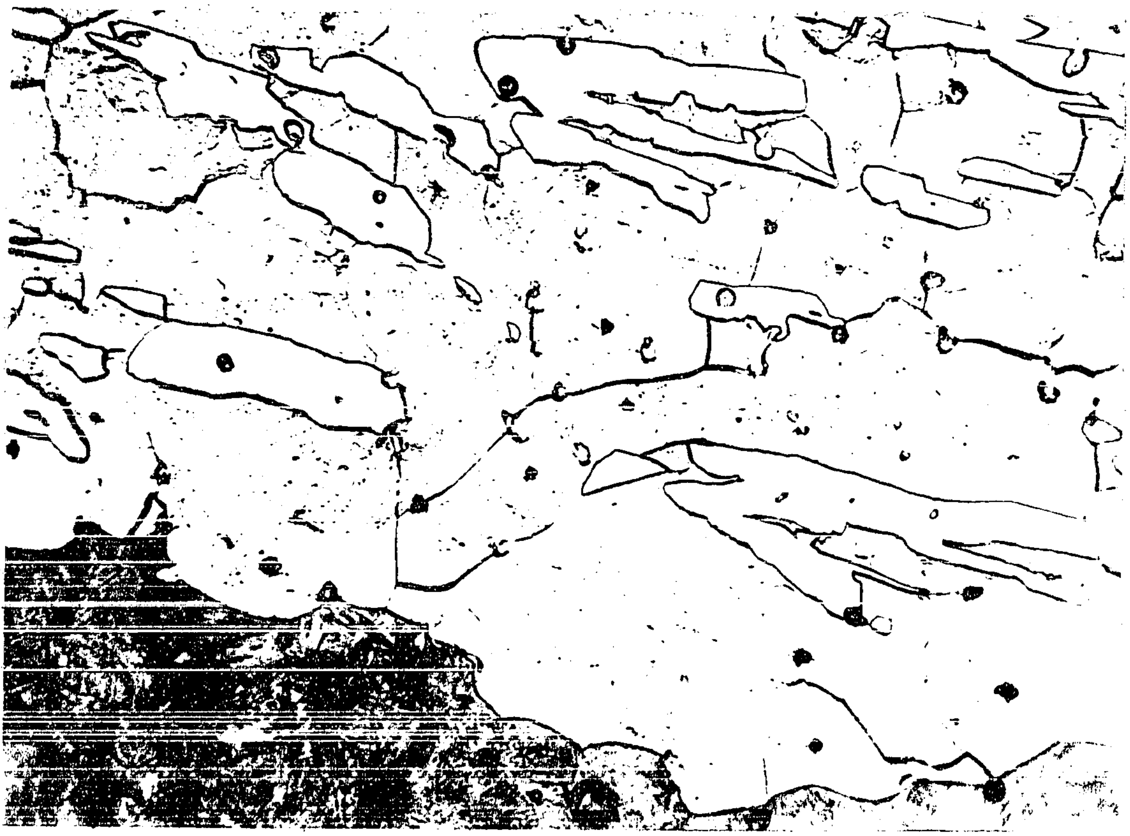


Figure 5a

Same as Figure 5 but a different section of the sample.

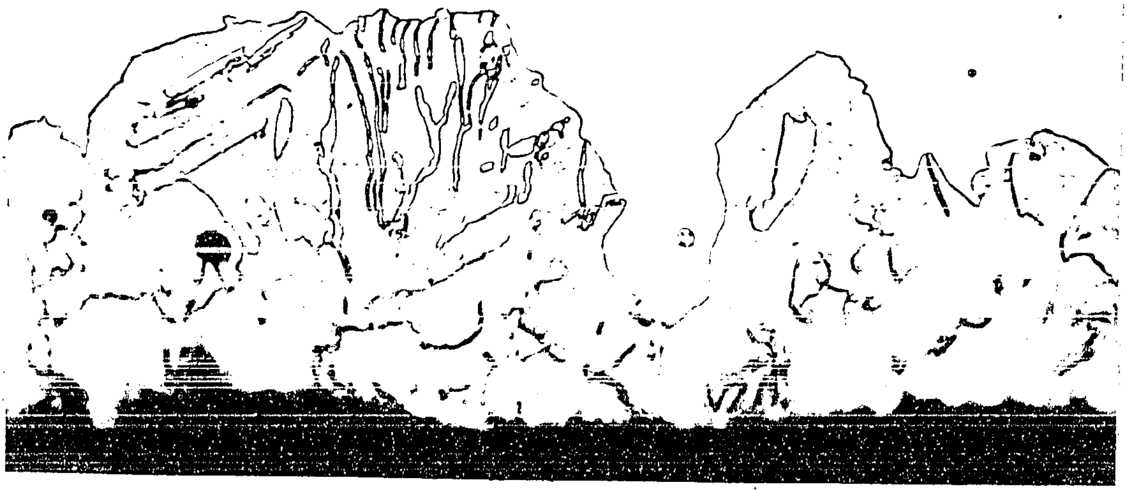


Figure 6
Sample No. 198
Isothermal transformation temperature 714°C
Time 11 minutes

Alpha Ferrite, Cementite, and Martensite

Shows transformation progressing at the edge. Also showed small cementite particles in center portion of the specimen.

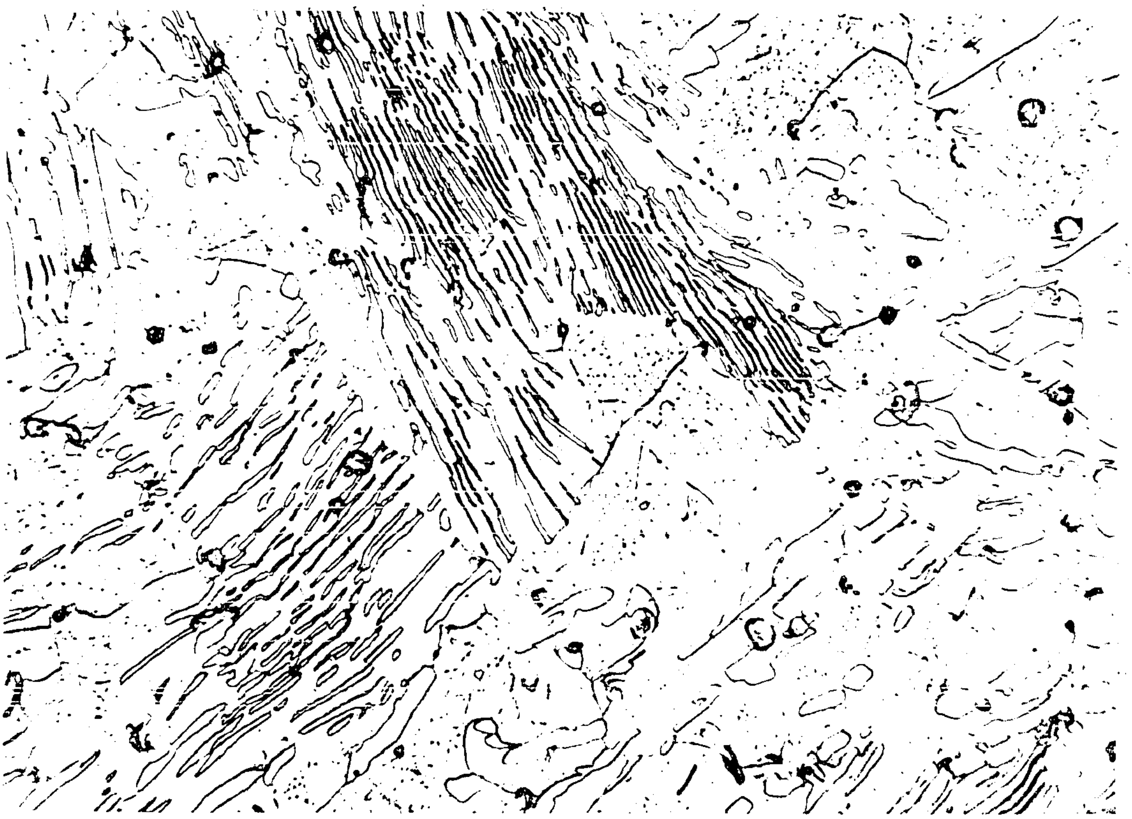


Figure 7
Sample No. I100
Isothermal transformation temperature 713°C
Time 51 minutes

Alpha Ferrite and Cementite with some present as pearlite

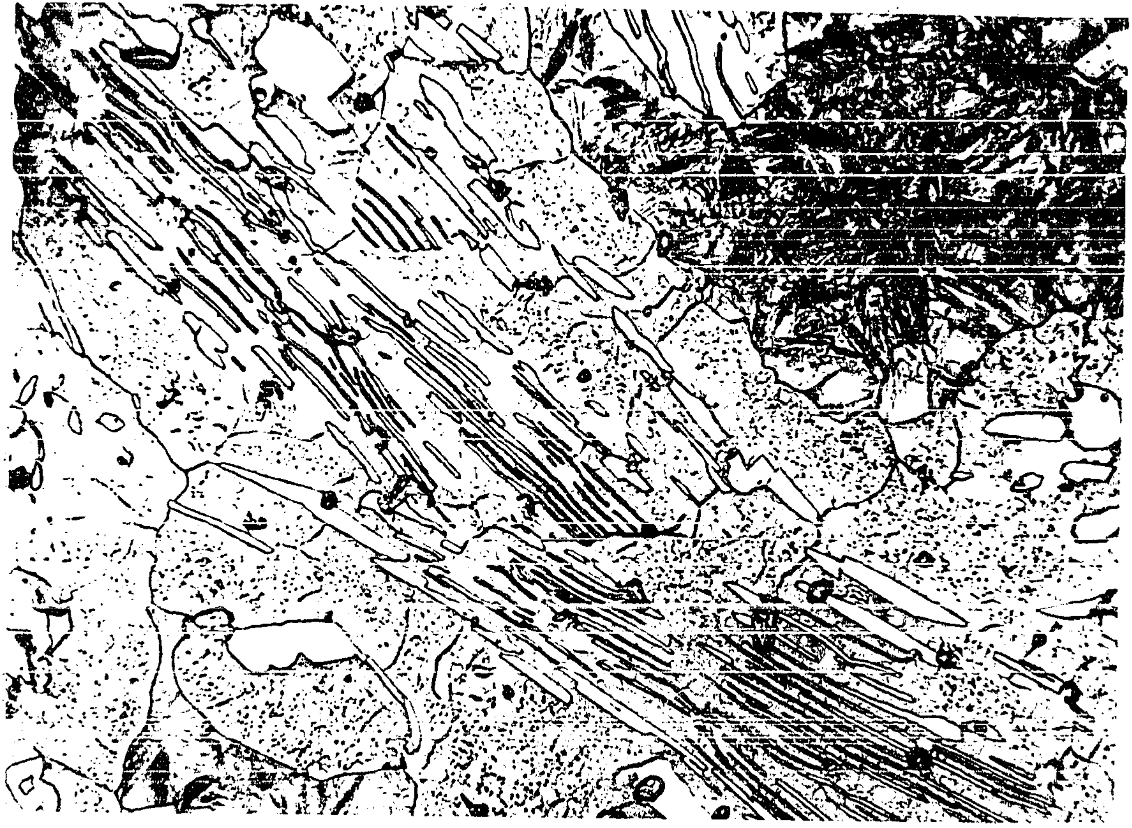


Figure 7a
Sample No. 1100
Isothermal transformation temperature 713°C
Time 51 minutes

Same as Figure 7 but a different portion of the specimen. A few sections, as illustrated here, revealed some austenite untransformed. This, as usual, is revealed by the martensite present.

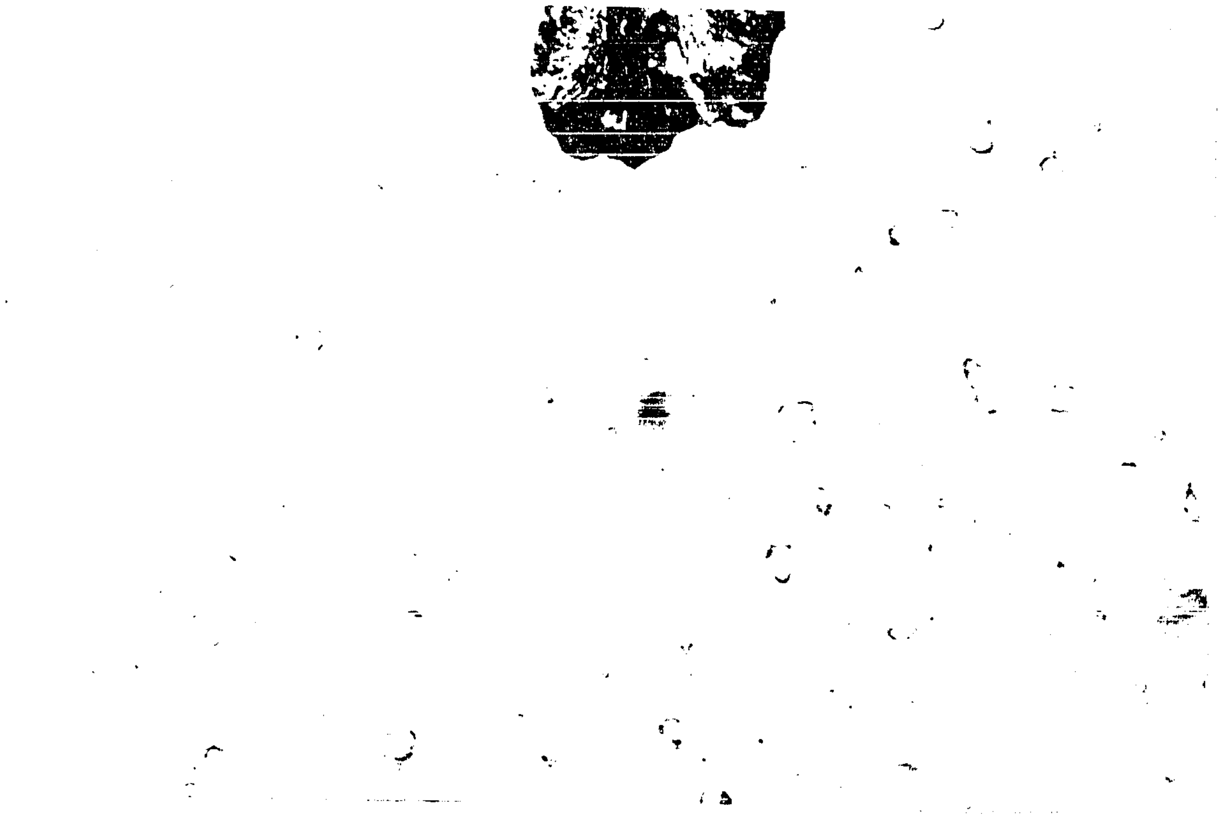


Figure 8
Sample No. I83
Isothermal transformation temperature 688°C
Time 12 seconds

Pearlite and Martensite

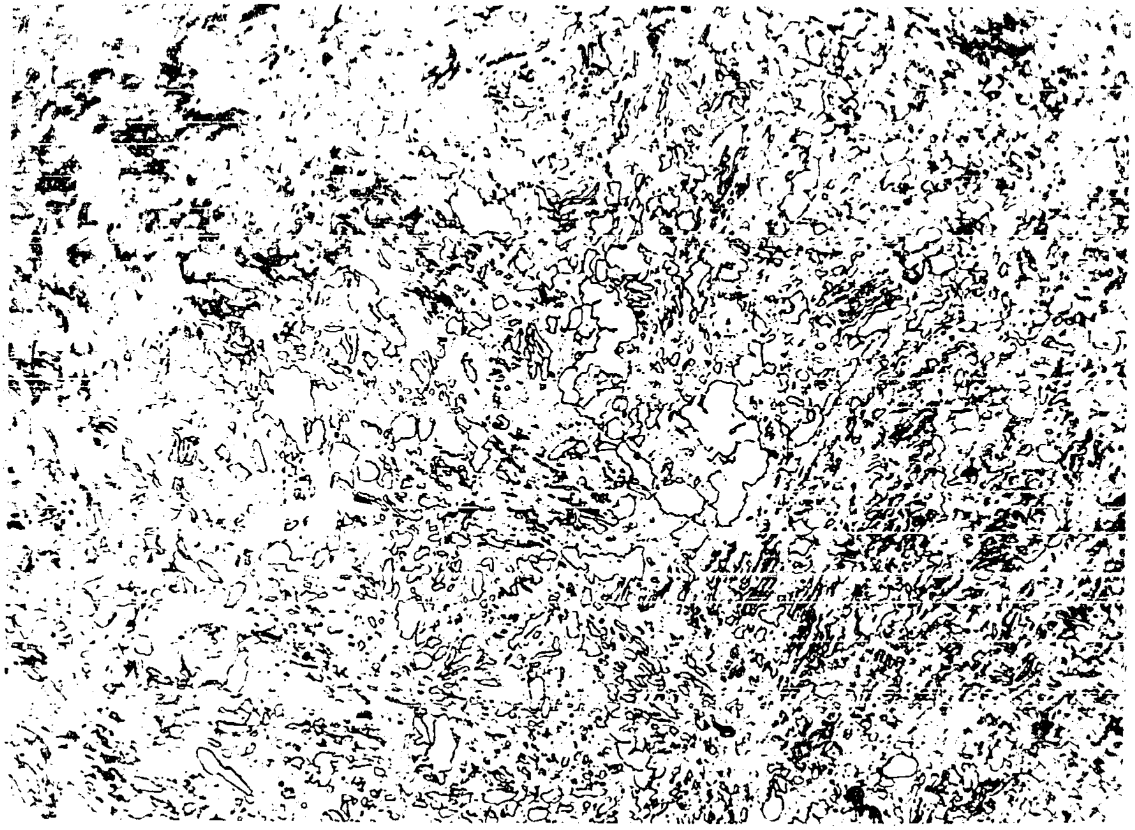


Figure 9
Sample No. I84
Isothermal transformation temperature 688°C
Time 80 seconds

Pearlite and Martensite

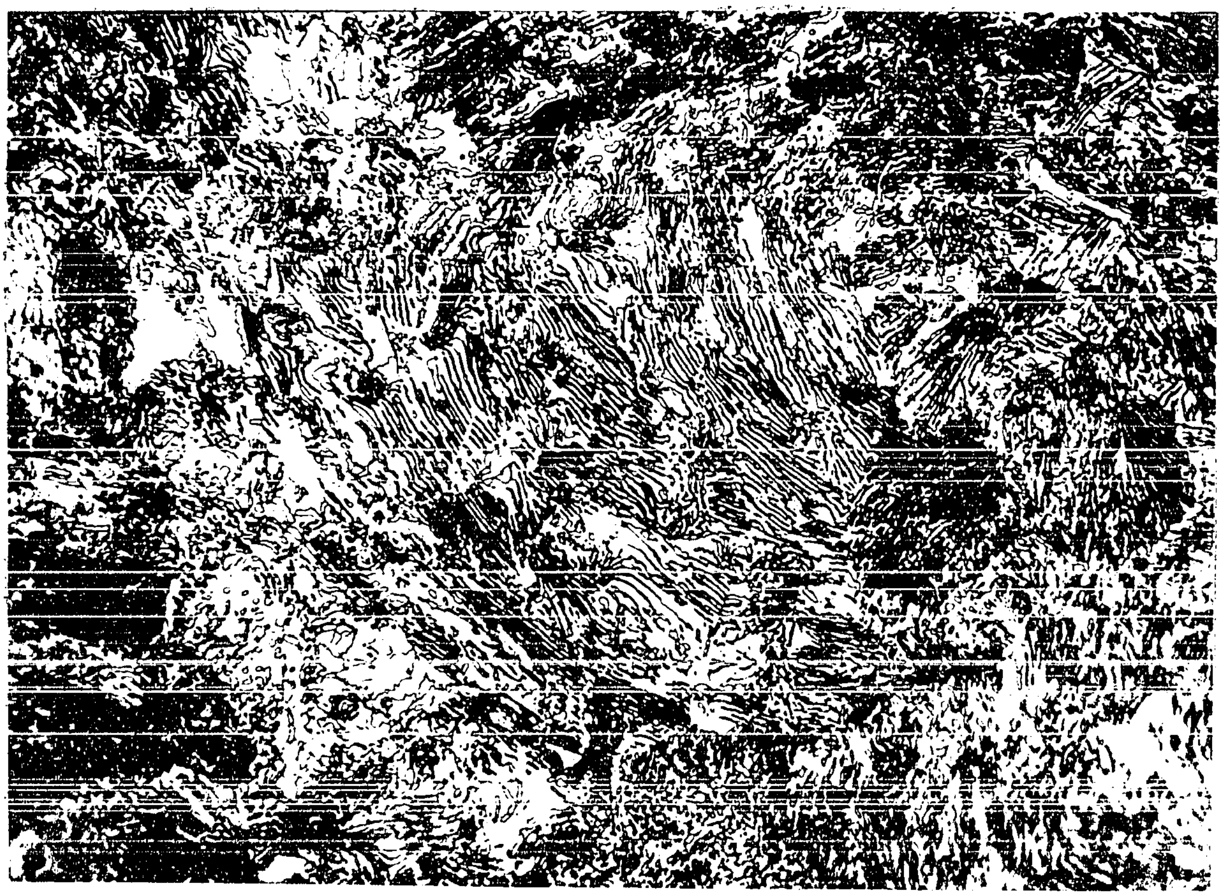


Figure 10
Sample No. 181
Isothermal transformation temperature 688°C
Time 90 seconds

Pearlite

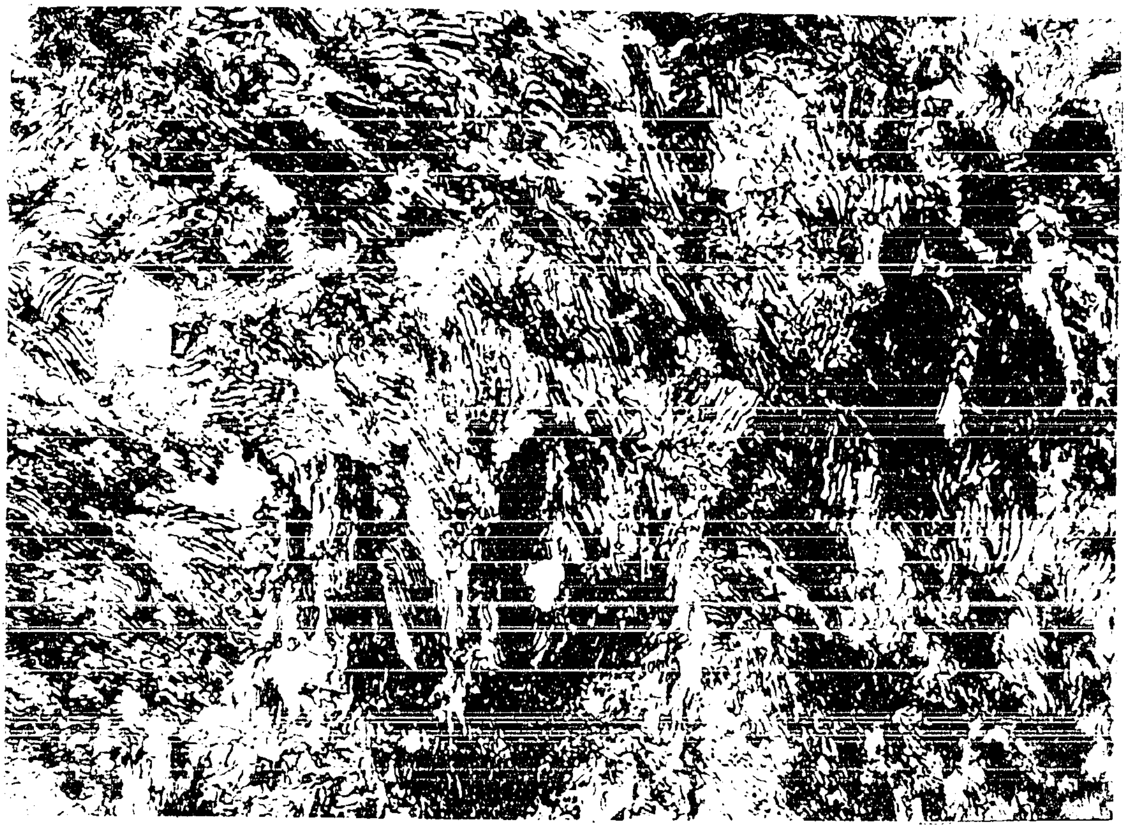


Figure 11
Sample No. 182
Isothermal transformation temperature 688°C
Time 15 minutes

Pearlite

Figure 12
Sample No. I85
Isothermal transformation temperature 688°C
Time 55 minutes

Alpha Ferrite, Spheroidized Cementite, and Pearlite

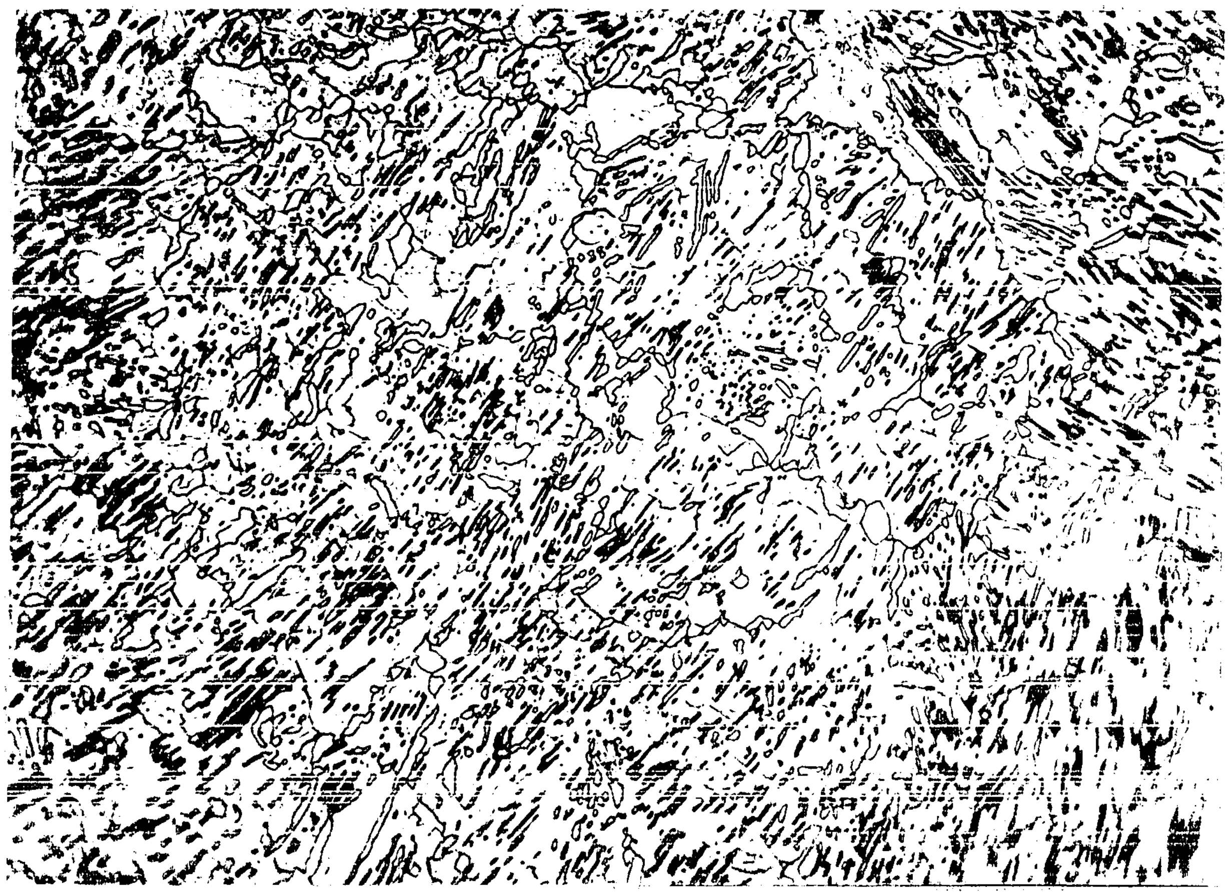


Figure 13
Sample No. 188
Isothermal transformation temperature 688°C
Time 93 minutes

Alpha Ferrite, Spheroidized Cementite, and Pearlite

Figure 14
Sample No. I9
Isothermal transformation temperature 676°C
Time 1 second

Pearlite and Martensite

Figure 15
Sample No. I10
Isothermal transformation temperature 676°C
Time 3 seconds

Pearlite and Martensite

Figure 16
Sample No. Ill
Isothermal transformation temperature 676°C
Time 6 seconds

Pearlite and Martensite

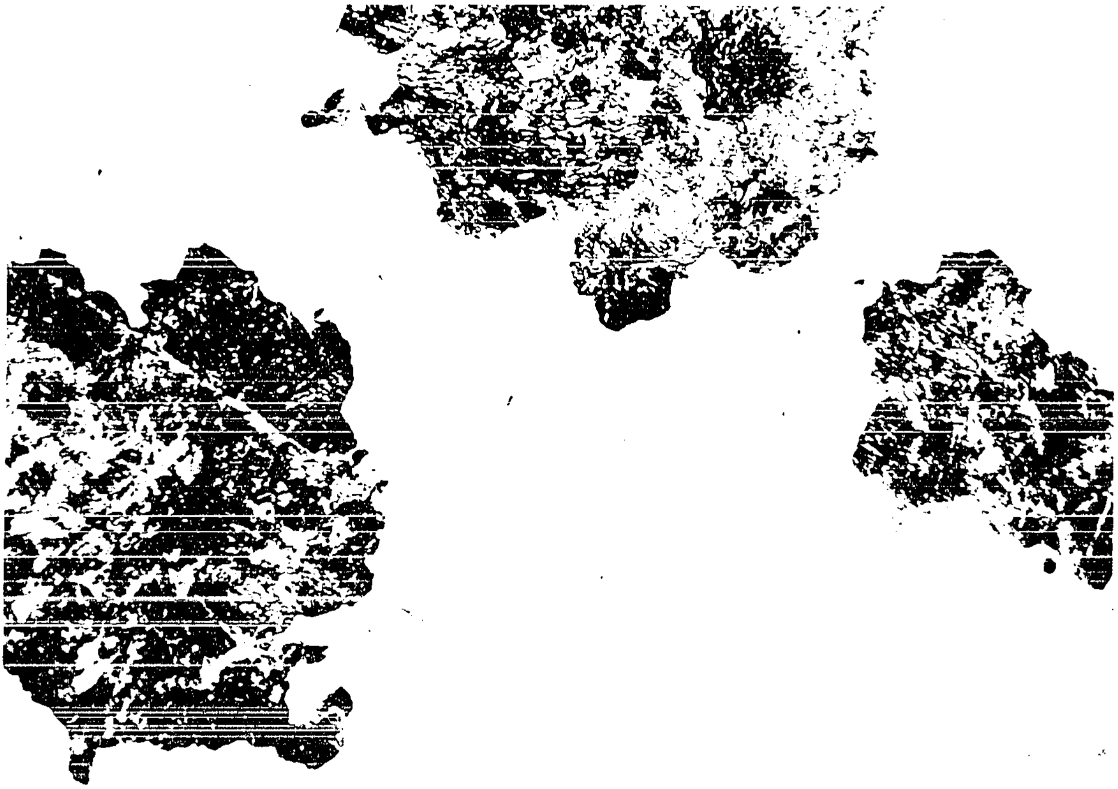


Figure 17
Sample No. I12
Isothermal transformation temperature 676°C
Time 8 seconds

Pearlite and Martensite

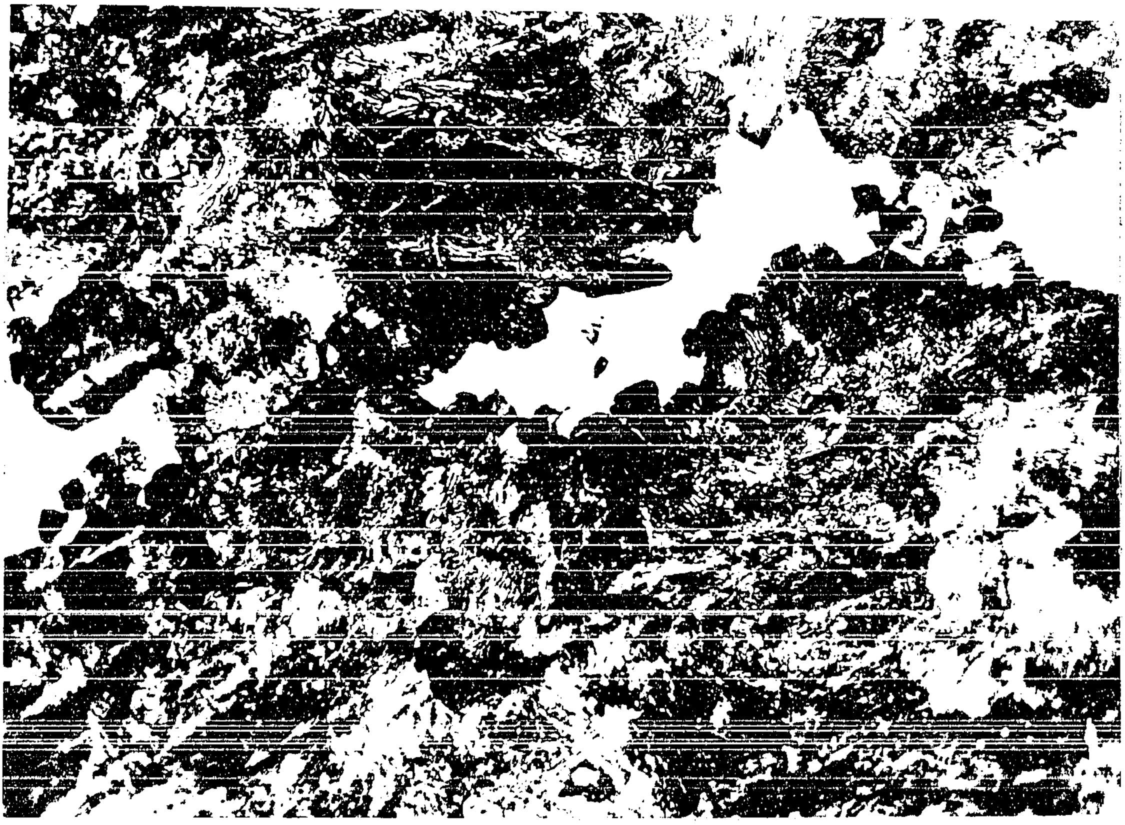


Figure 18
Sample No. 113
Isothermal transformation temperature 676°C
Time 10 seconds

Pearlite and Martensite

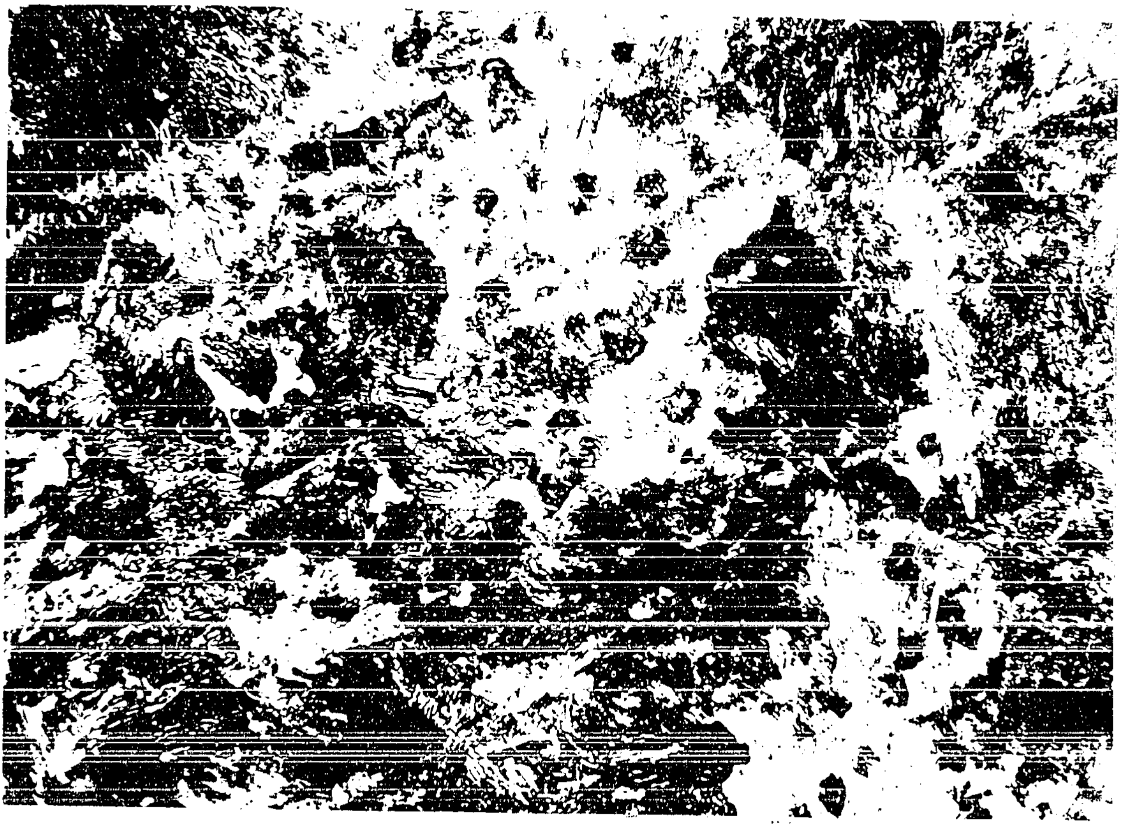


Figure 19
Sample No. I14
Isothermal transformation temperature 676°C
Time 15 seconds

Pearlite and a very small

amount of Martensite

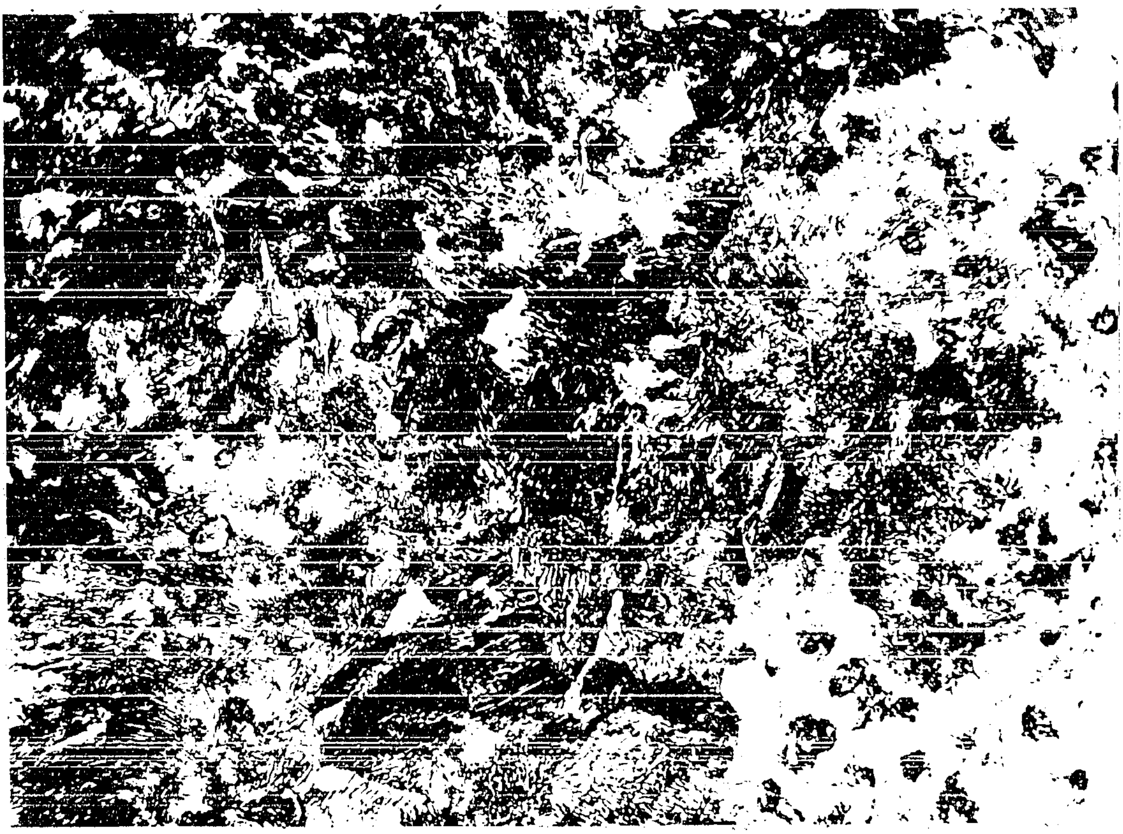


Figure 20
Sample No. I5
Isothermal transformation temperature 676°C
Time 20 seconds

Pearlite

Figure 21
Sample No. 165
Isothermal transformation temperature 353°C
Time 30 seconds

Bainite and Martensite

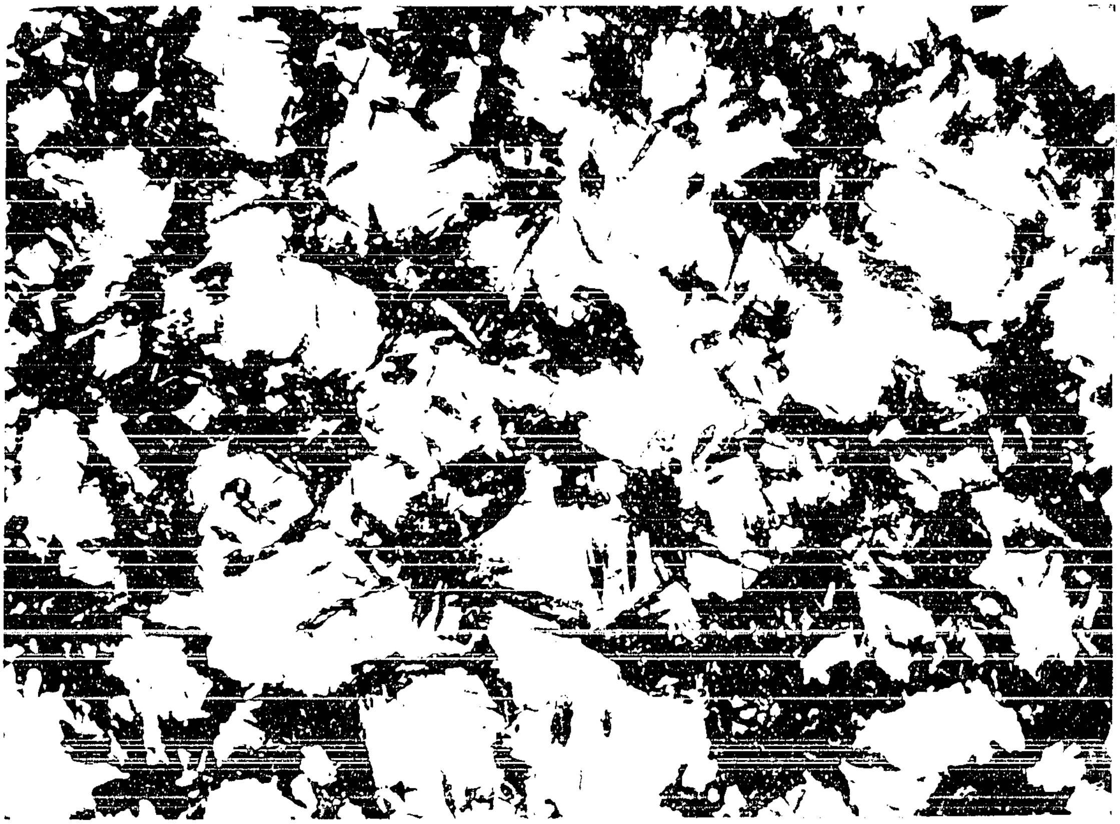


Figure 22
Sample No. I66
Isothermal transformation temperature 353°C
Time 130 seconds

Bainite and Martensite

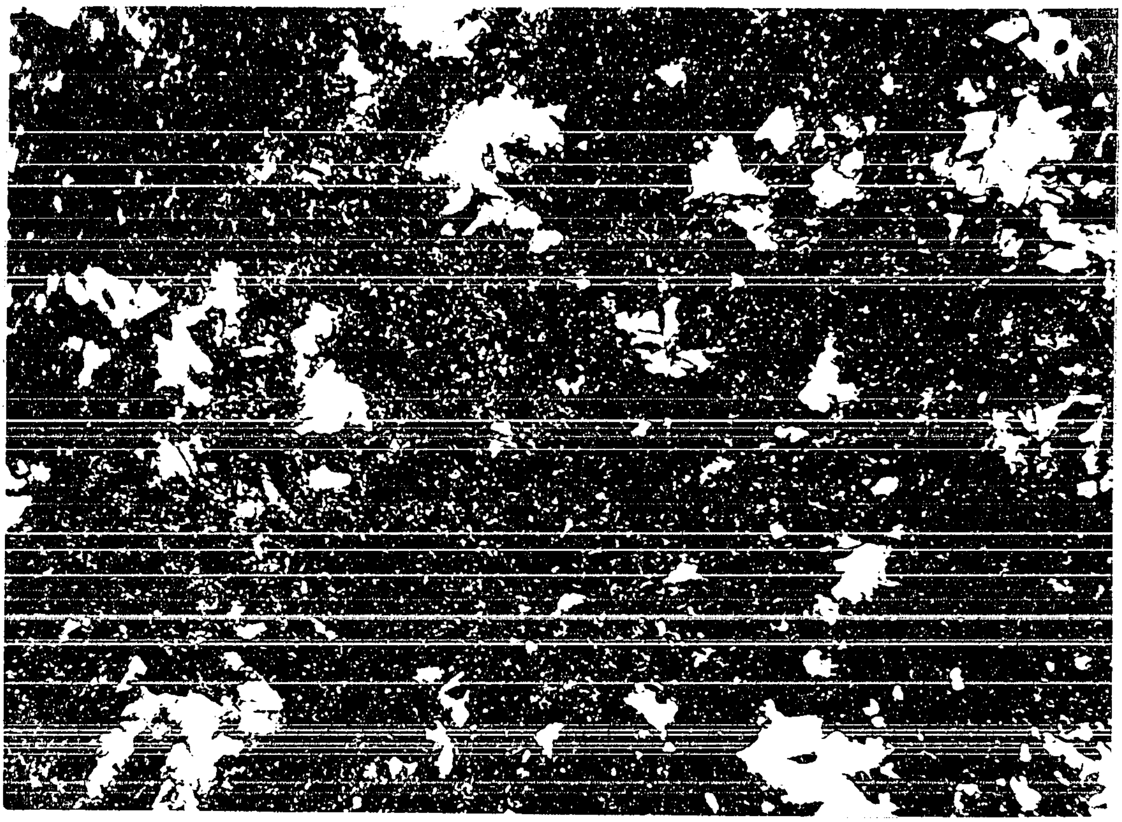


Figure 23
Sample No. 167
Isothermal transformation temperature 353°C
Time 160 seconds

Bainite and Martensite

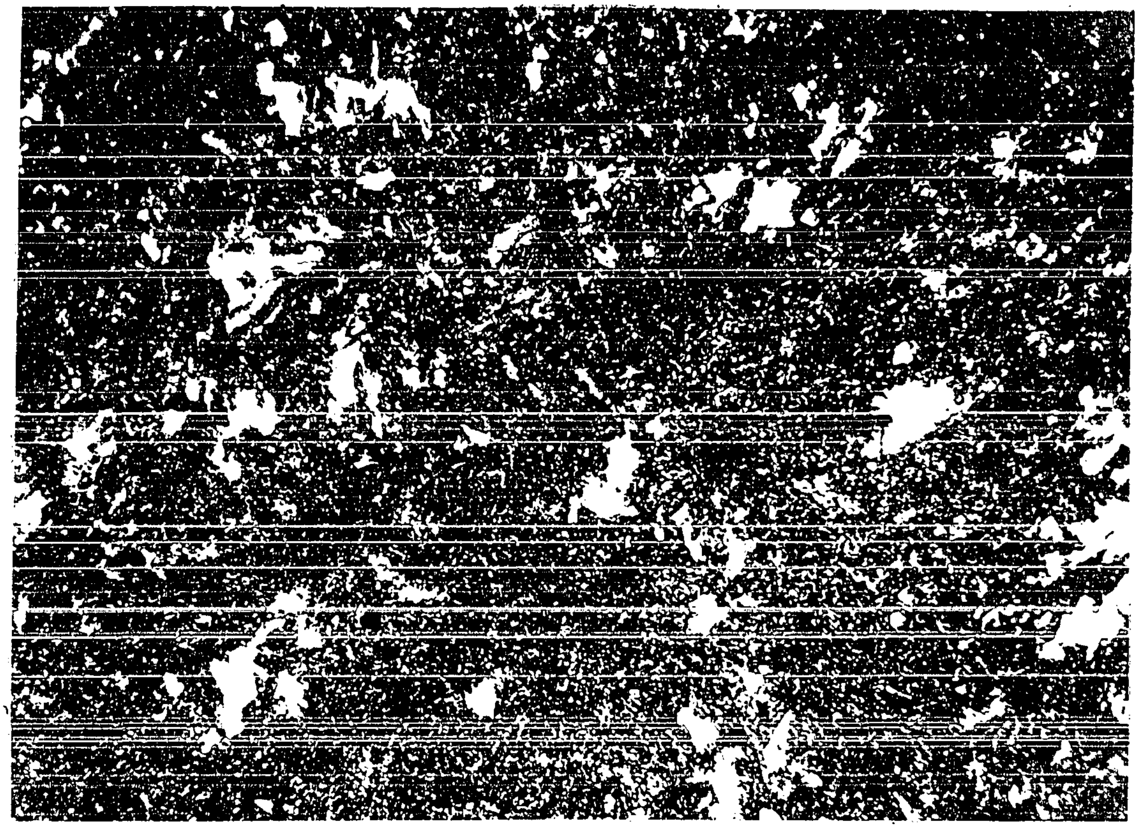


Figure 24
Sample No. 169
Isothermal transformation temperature 353°C
Time 195 seconds

Bainite and Martensite

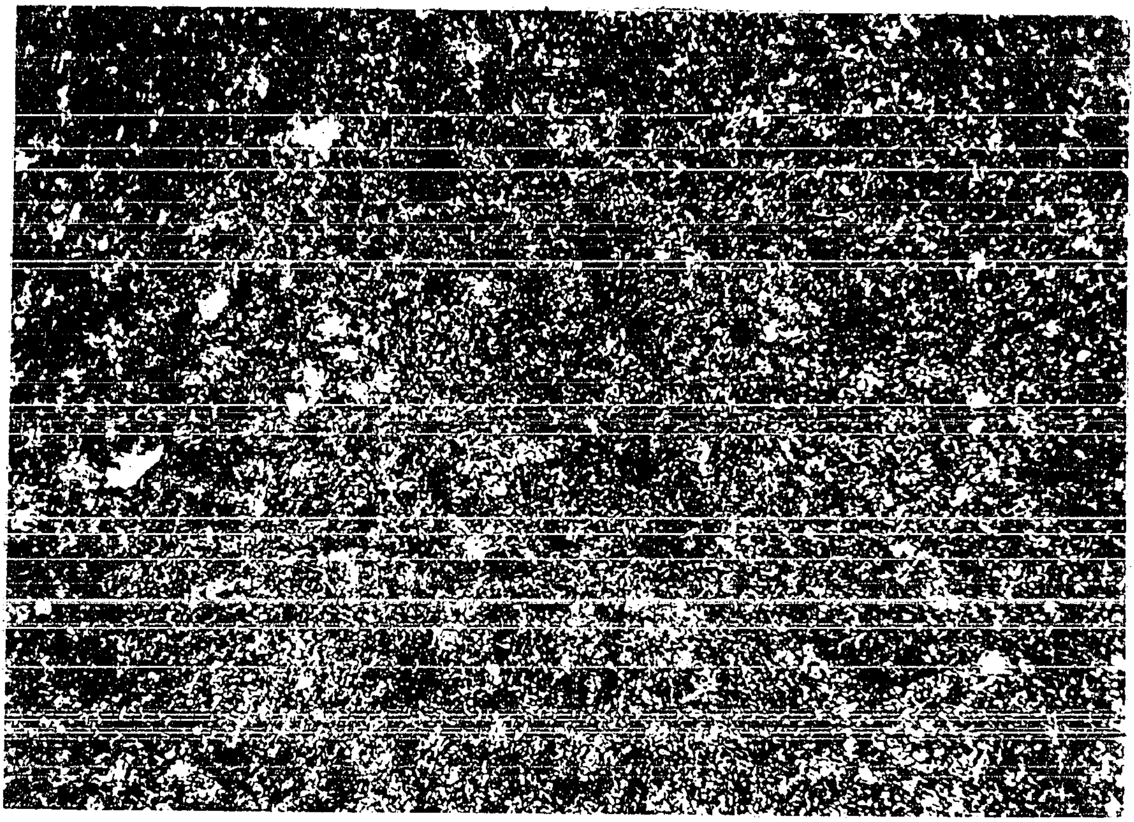


Figure 25
Sample No. I70
Isothermal transformation temperature 353°C
Time 225 seconds

Bainite and a small amount of Martensite

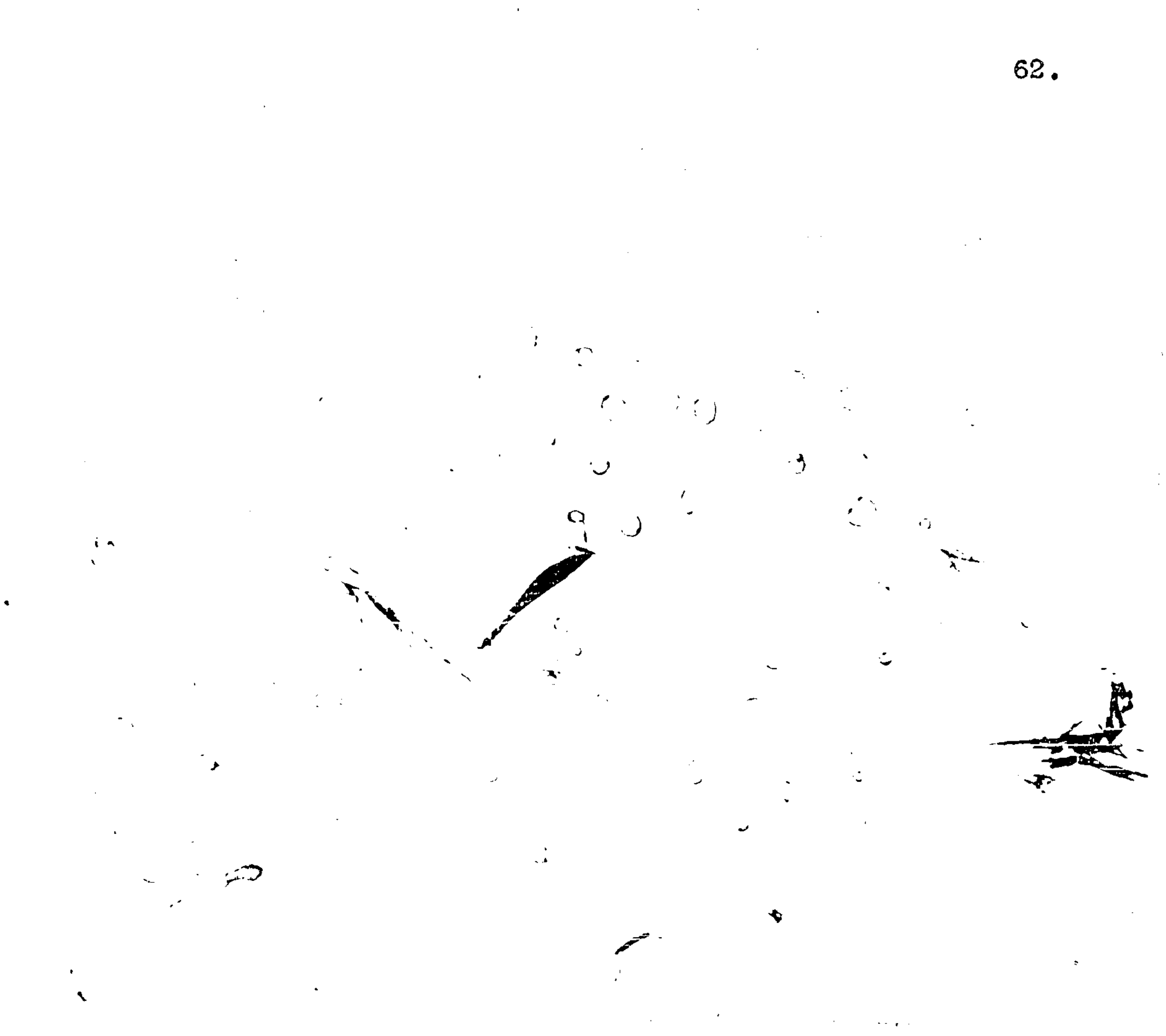


Figure 26
Sample No. 177
Isothermal transformation temperature 244°C
Time 5 minutes

Bainite and Martensite

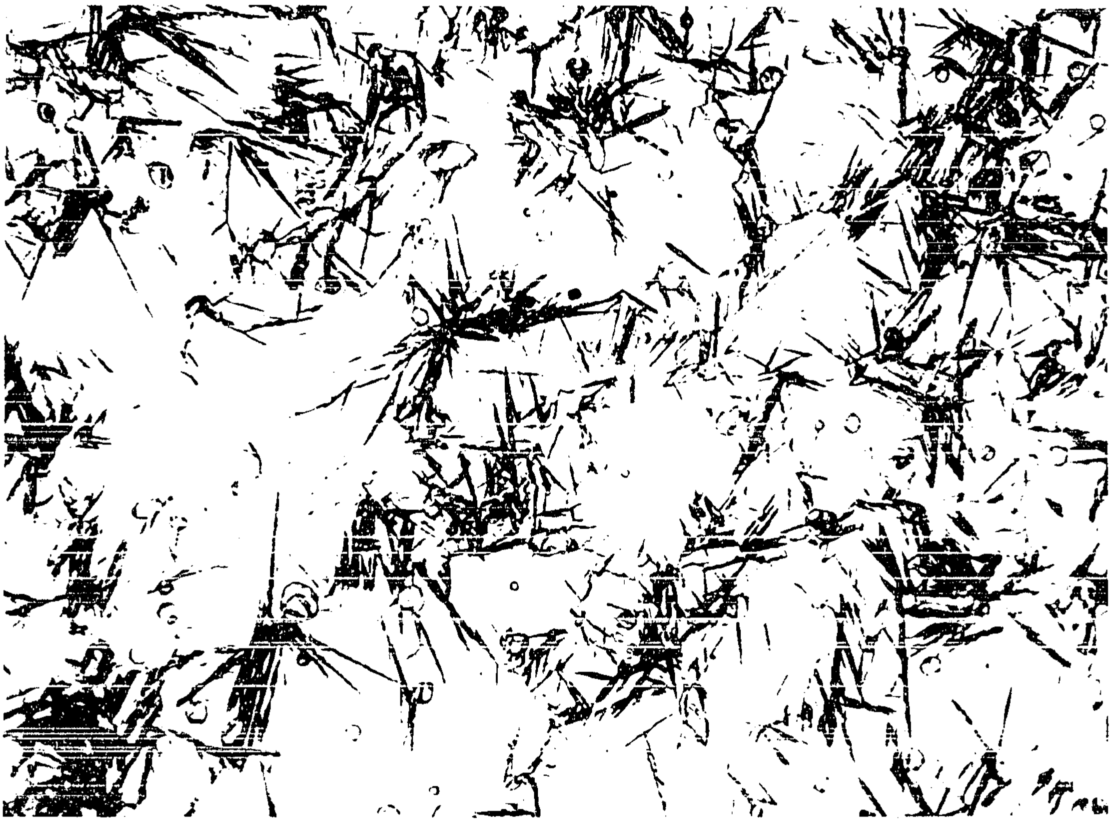


Figure 27
Sample No. 179
Isothermal transformation temperature 244°C
Time 15 minutes

Bainite and Martensite

Figure 28
Sample No. I78
Isothermal transformation temperature 244°C
Time 50 minutes

Bainite

Figure 29
Sample No. I1
Quenching Temperature 242°C Time 13 seconds
Tempering Temperature 270°C Time 10 seconds

Tempered and Untempered Martensite

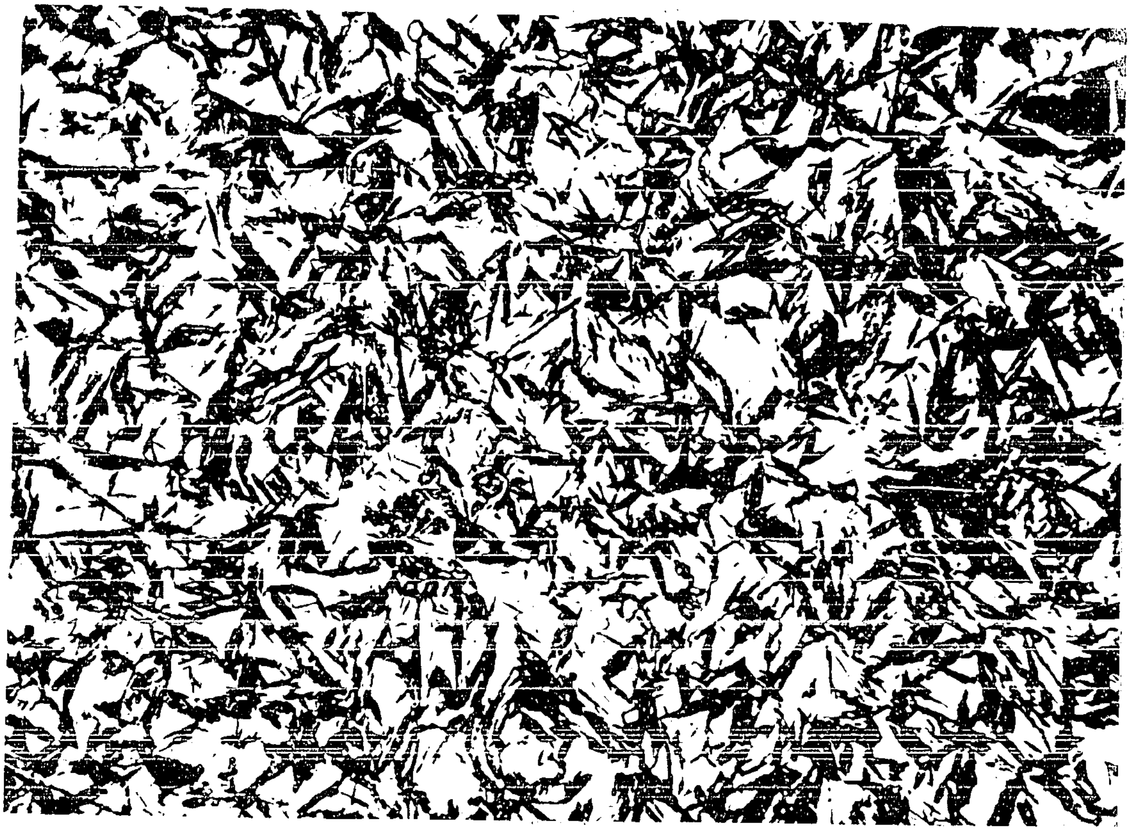


Figure 30
Sample No. 145
Quenching Temperature 175°C Time 10 seconds
Tempering Temperature 283°C Time 5 seconds

Tempered and Untempered Martensite

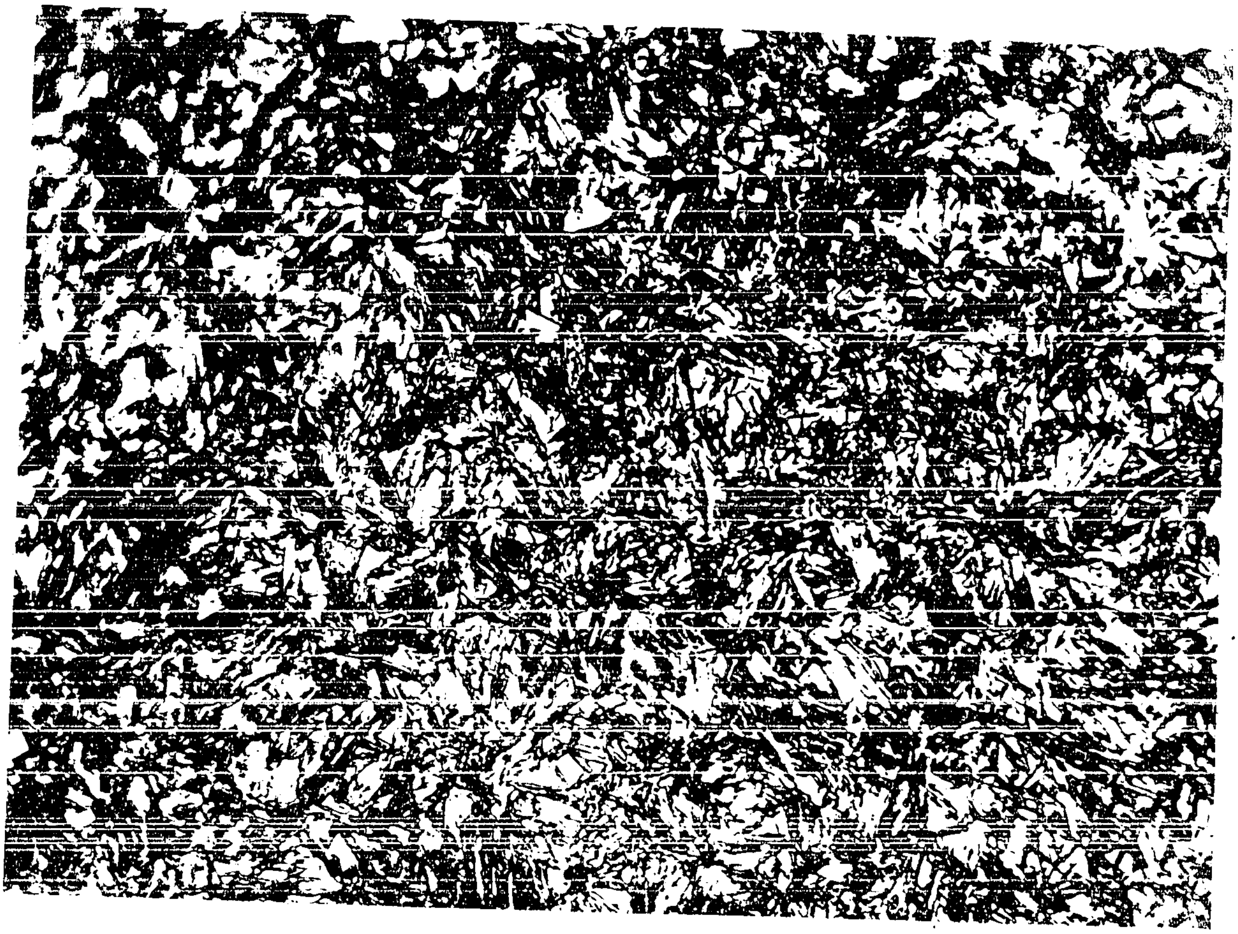


Figure 31
Sample No. 147
Quenching Temperature 126°C Time 10 seconds
Tempering Temperature 282°C Time 5 seconds

Tempered and Untempered Martensite

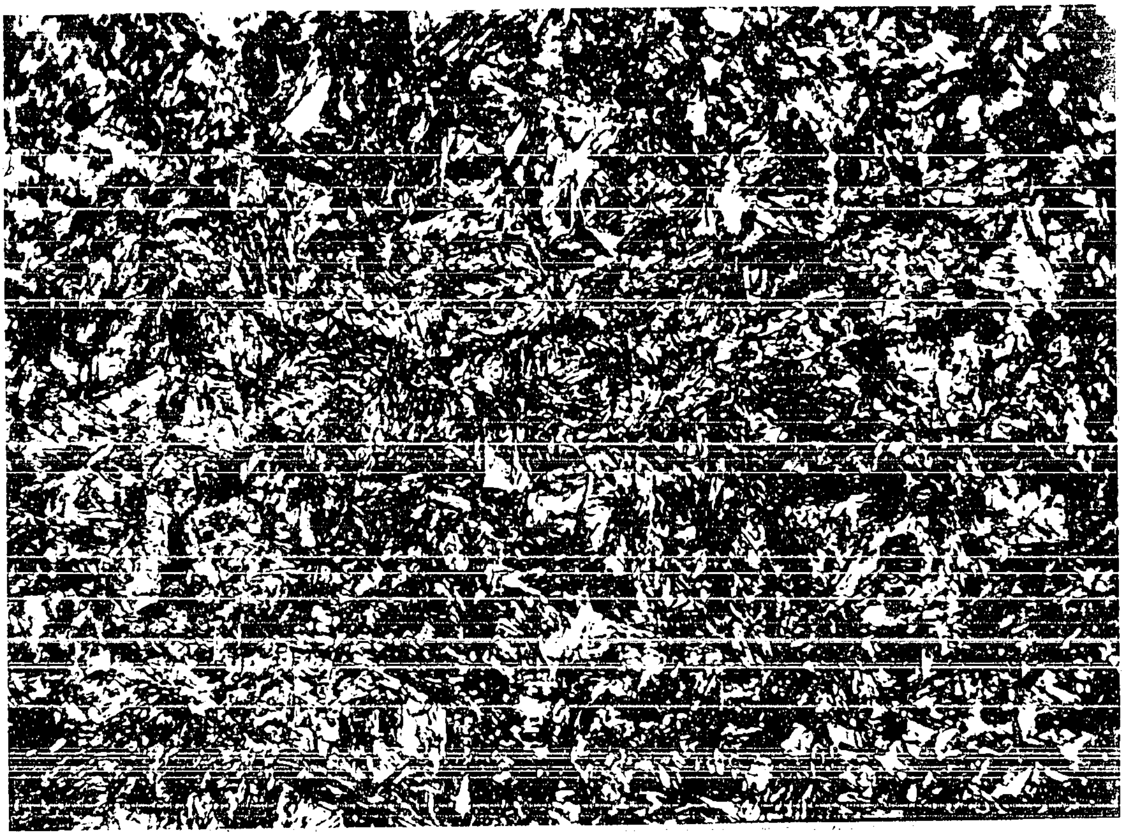


Figure 32
Sample No. I49
Quenching Temperature 108°C Time 10 seconds
Tempering Temperature 283°C Time 5 seconds

Tempered and Untempered Martensite

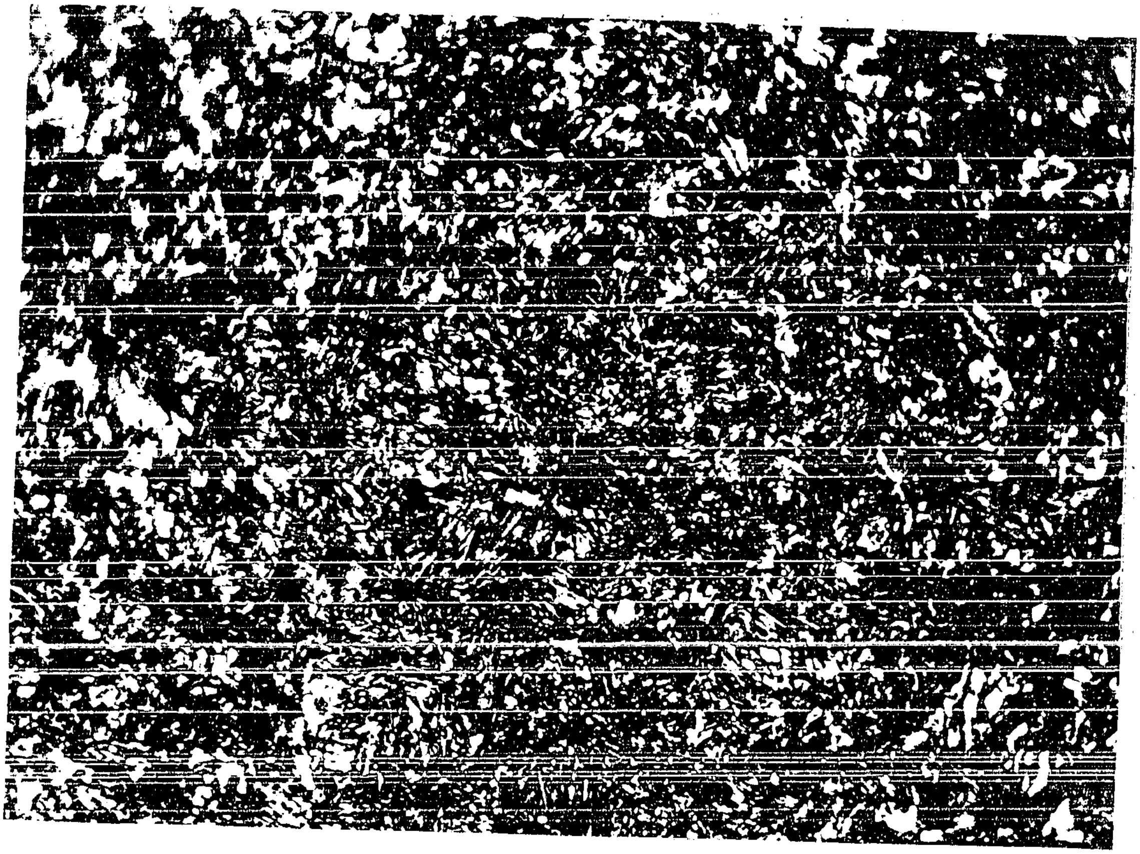


Figure 33
Sample No. 150
Quenching Temperature 96°C Time 10 seconds
Tempering Temperature 282°C Time 5 seconds

Tempered Martensite and a very small amount
of Untempered Martensite

THE FORMATION OF AUSTENITE IN IRON-CARBON POWDER PRODUCTS

A few studies were made of the formation of austenite in the 0.87-0.89%C iron-carbon alloys that were prepared. Samples in the condition shown in Figure (3) were quenched in a lead pot for the times and at the temperatures desired. Figures (34), (35) and (36) show the structures resulting when taken to 728°C for 30 secs, 97 minutes, and 14 1/2 hours respectively. After the times indicated at 728°C the samples were quenched rapidly to room temperature and then prepared for microscopic examination. Figures (37) and (38) show results obtained for like samples taken to 724°C for 38 seconds and 19 hours respectively. Some samples were also run in a like manner at lower temperatures. The structures of samples heated at 713°C for 8 minutes and 68 minutes are shown in Figures (39) and (40) while one heated at 716°C for 200 seconds is shown in Figure (41).

The above results show that the complete formation of austenite is very rapid at 728°C as compared to 724°C. The results at temperatures as low as 713°C indicate either segregation due possibly to oxygen or nitrogen or that austenite formation may start at such a low temperature. Further work is definitely required before conclusions may be reached.

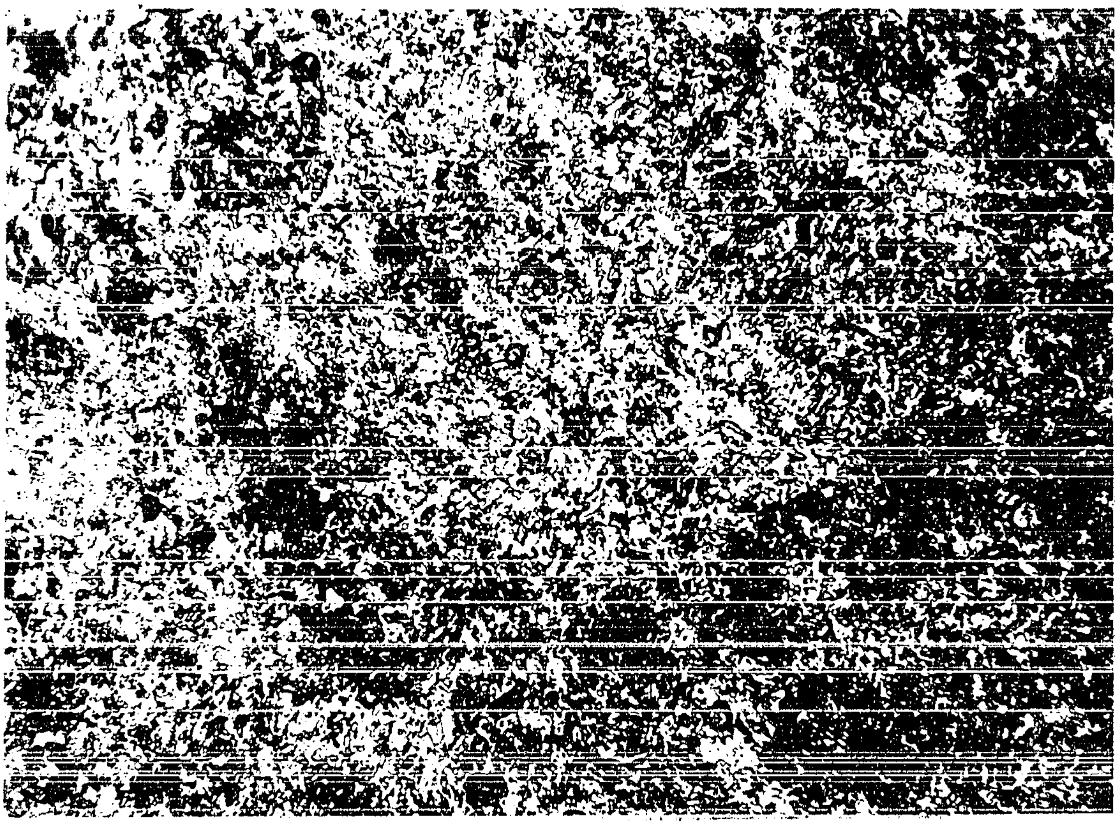


Figure 34
Sample No. I109
Austenitizing Temperature 728°C
Time 30 seconds

Martensite and fine carbides

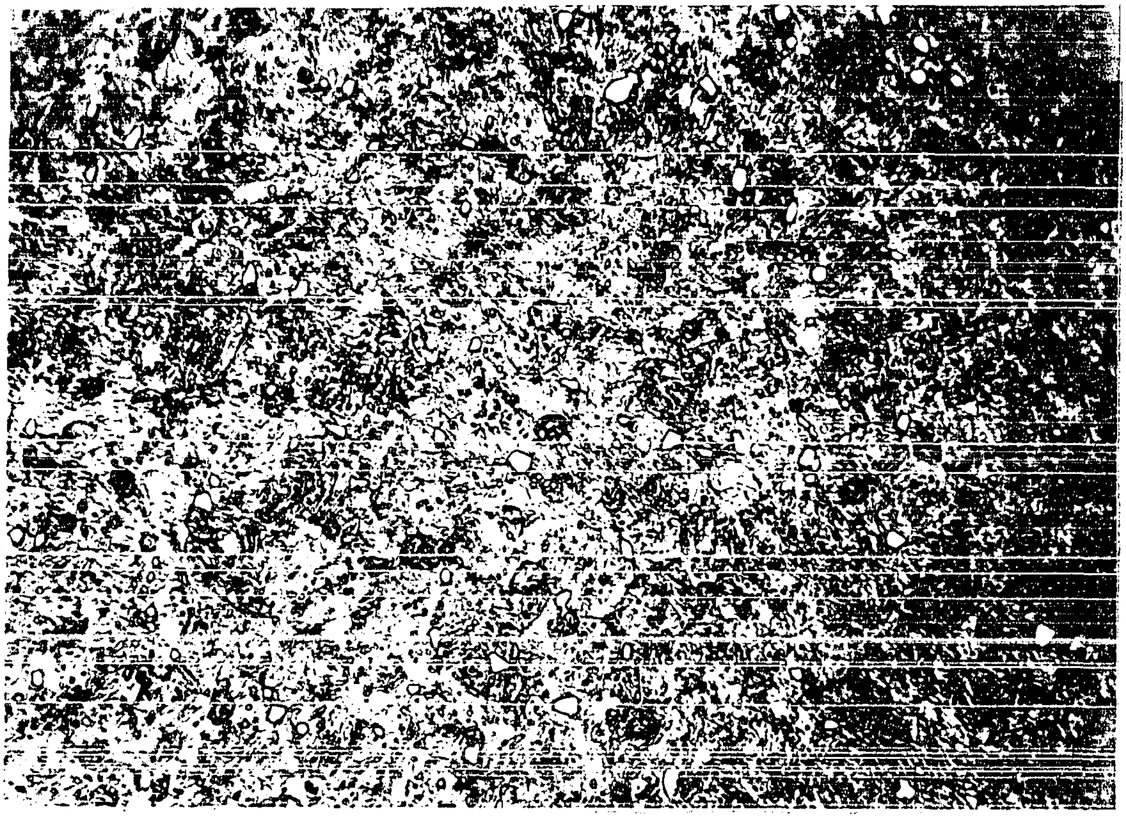


Figure 35
Sample No. I110
Austenitizing Temperature 728°C
Time 97 minutes

Martensite and Cementite

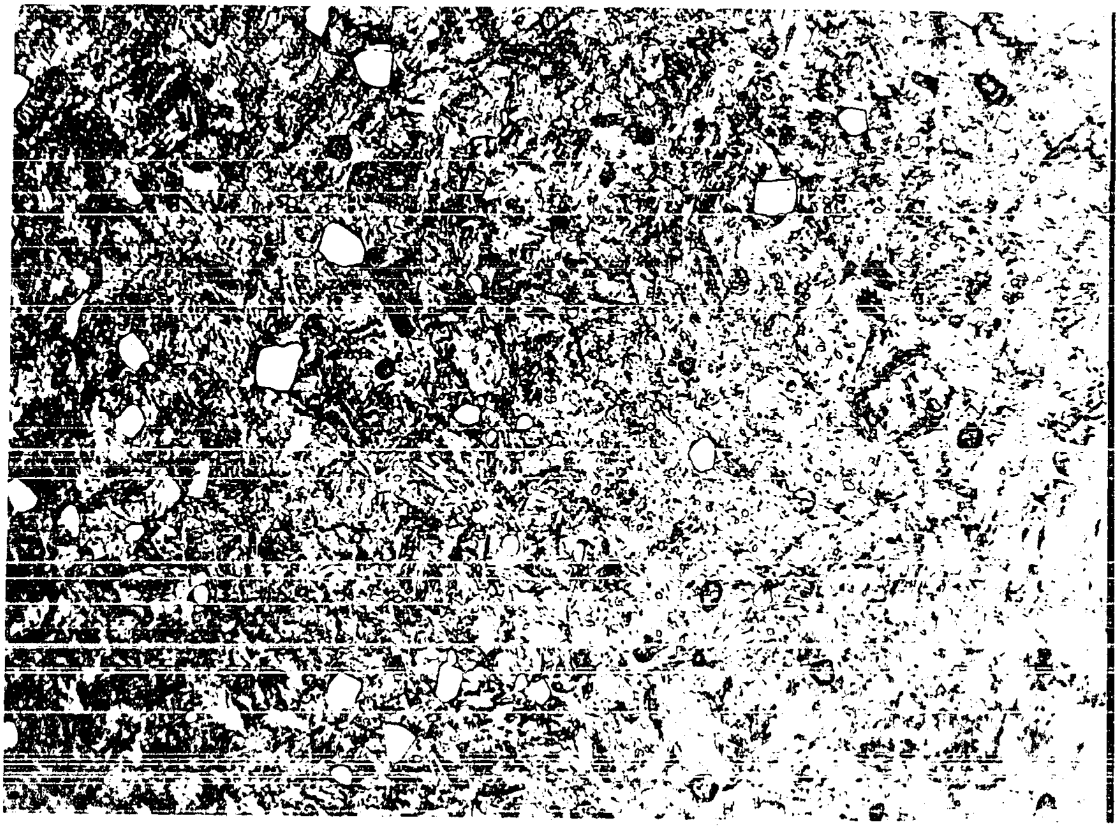


Figure 36
Sample No. I120
Austenitizing Temperature 728°C
Time 14 1/2 hours

Martensite and Cementite

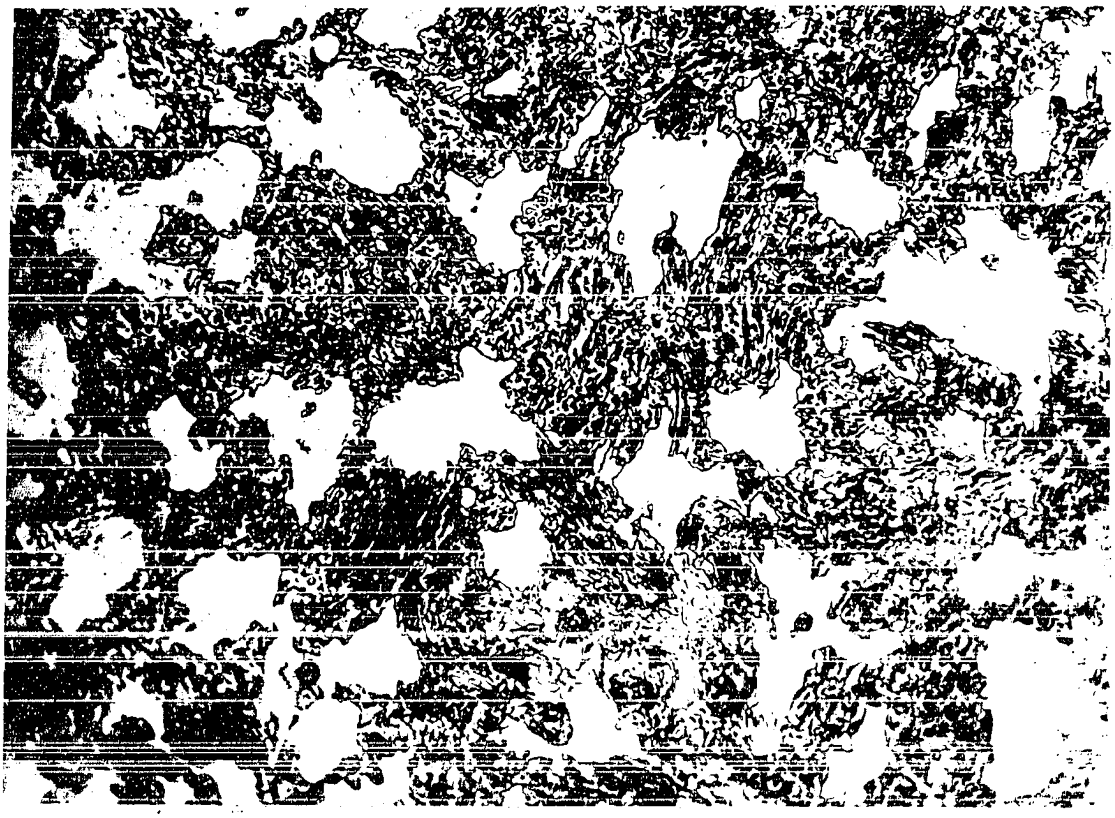


Figure 37
Sample No. I114
Austenitizing Temperature 724°C
Time 38 seconds

Martensite, Cementite and Alpha Ferrite

Figure 38
Sample No. I119
Austenitizing Temperature 724°C
Time 19 hours

Martensite, Ferrite, and Cementite

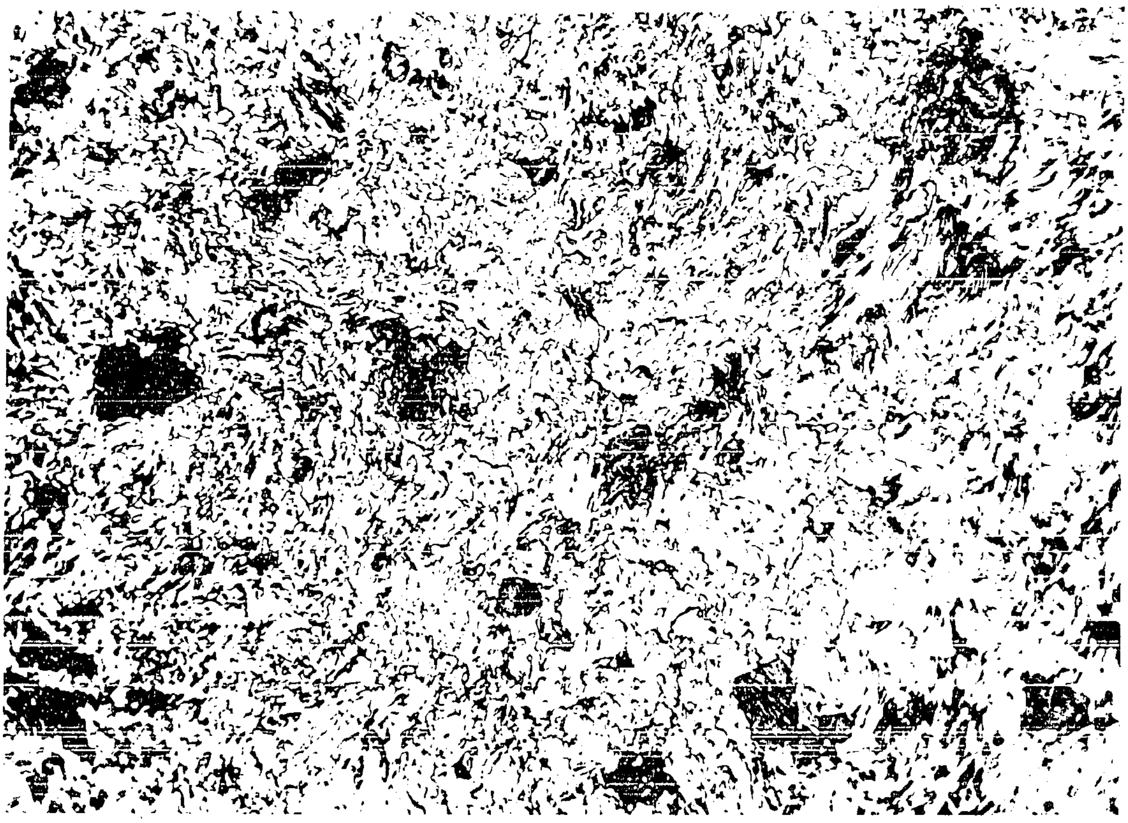


Figure 39
Sample No. 197
Austenitizing Temperature 713°C
Time 8 minutes

Martensite, Cementite and Alpha Ferrite

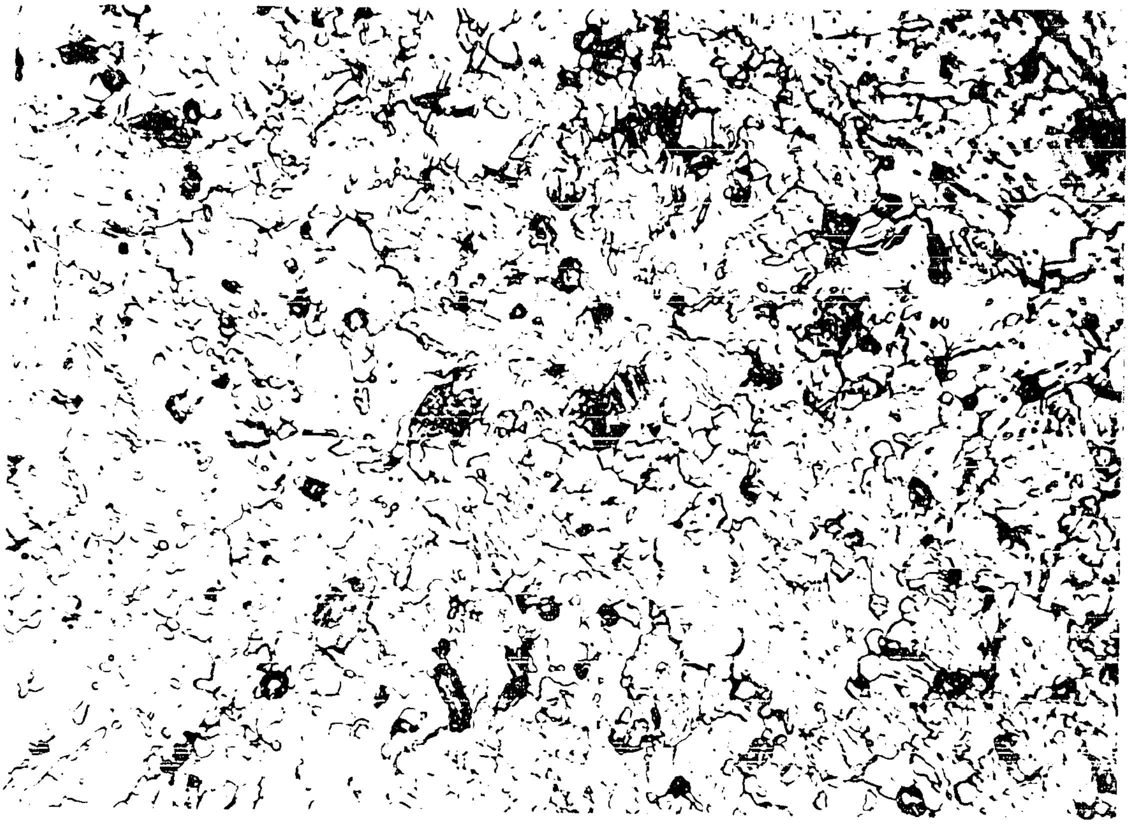


Figure 40
Sample No. 199
Austenitizing Temperature 713°C
Time 68 minutes

Martensite, Cementite, and Alpha Ferrite

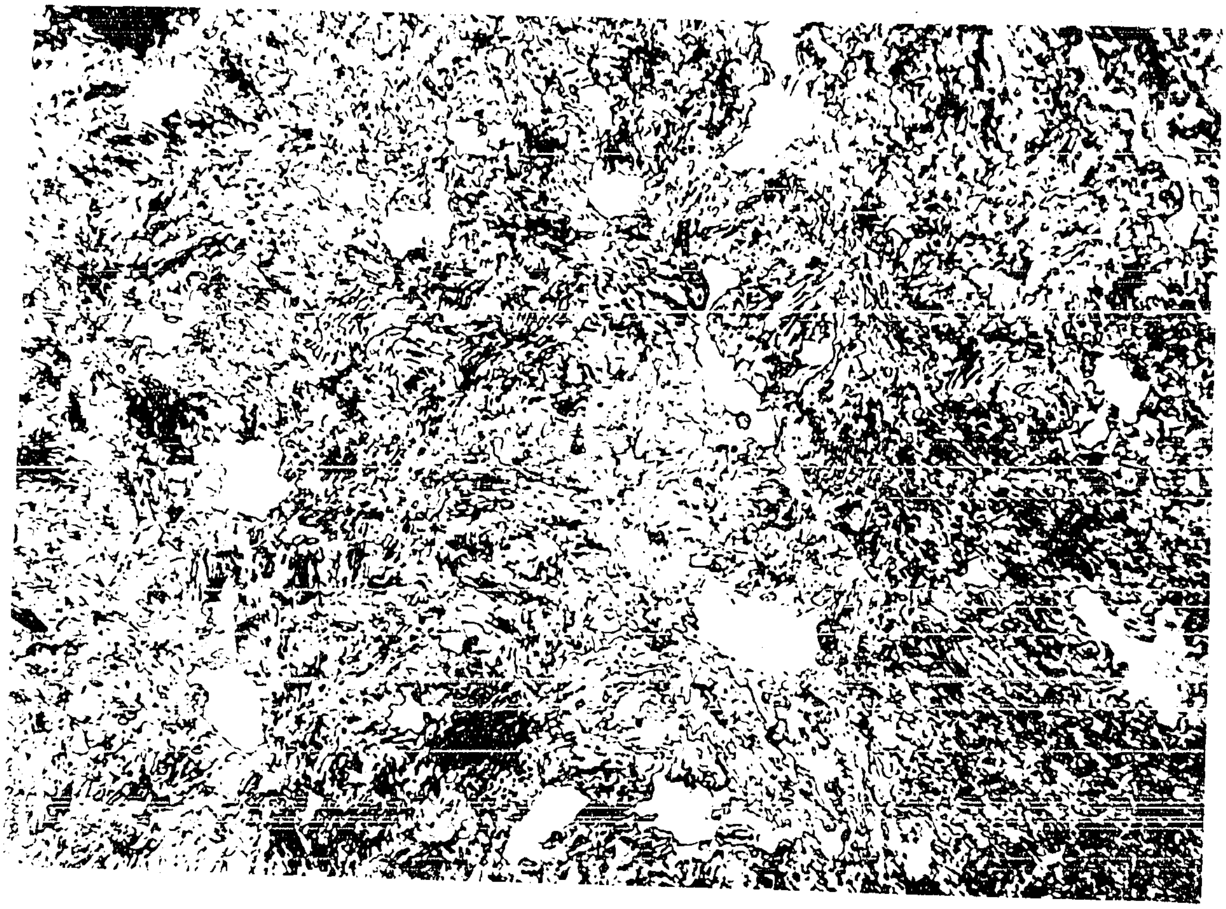


Figure 41
Sample No. I105
Austenitizing Temperature 716°C
Time 200 seconds

Martensite, Cementite, and Alpha Ferrite

PACK CARBURIZING STUDIES OF IRON POWDER COMPACTS

Earlier in this presentation comments were made pertaining to the method used for preparation of iron-carbon alloys by carburizing pure iron compacts in hardwood charcoal. Before this procedure was decided upon other experiments had been performed which yielded interesting results:

Carburizing with Energized Charcoal

The samples that were prepared for isothermal transformation studies of austenite decomposition were all carburized in ordinary hardwood charcoal. Samples carburized in this manner tend to reach what one might easily consider a maximum carbon content. For example, at 925°C a 0.15 gram sample of carbonyl iron "L" pressed at 25,000 psi will reach an average carbon content of 1.25%C after 50 hours carburizing time. The rate of carbon pick-up is slow after about an hour at temperature. On the other hand, the carbon absorption is very rapid and reaches high values when energized charcoal is used.

In these experiments sodium carbonate was used as an energizer. The energized charcoal was prepared by first dissolving Na_2CO_3 in an amount of water just sufficient to dampen thoroughly the quantity of charcoal used. The amount of energizer added was equal to 10% of the weight of the charcoal. The moistened charcoal after thorough mixing was dried at 150°C. After drying it was used in a double carburizing tube exactly as in previous studies with ordinary hardwood charcoal.

It was found that with energized charcoal carburizing proceeds very rapidly to extremely high carbon contents and that carbon absorption in appreciable amounts may occur at low temperatures.

Carbon absorption was followed primarily by weight changes and supplemented with microscopic examination and chemical analysis. Table II shows some of the results of energized charcoal studies on carbonyl iron "L", electrolytic iron (as plated), ingot iron, tungsten powder compacts, and titanium powder compacts. The carbonyl iron "L" compacts weighed of the order of 0.2 gram and were 1/4" in diameter. The specimens of electrolytic iron varied in thickness and in shape and as a result there is a fair variation in average percentage weight increase. The tungsten and titanium powders were pressed as received from the manufacturers. They were not checked for oxygen or moisture contents. It is very likely therefore that the actual carbon contents are higher than the values listed as percentage weight increases.

In order to gain a clearer picture of the significance of the percentage weight increase, it may be stated that for short carburizing times and in cases where the temperature is low this percentage value may be at variance with the actual carbon content. For example, samples Nos. 3 and 4 of Table II showed an actual carbon analysis of 5.5%C. Further, sample no. 27 after pressing weighed 0.19525 grams and after carburizing weighed 0.19659 g. This sample was then heated to 1065°C for ten minutes in the neutral nitrogen atmosphere referred to earlier. The final weight was 0.19638. If it is assumed that the oxygen leaves as carbon monoxide, then the final carbon content of the compact is about 0.58% and the carbon picked up in carburizing is 0.62%. These values are based on the assumption that there is no oxygen present in the original powder. Both values should probably be about 0.07% higher. In another experiment the following data were obtained when carbonyl iron "L" was carburized with energizer at 650°C for two hours:

Sample No.	Weight after pressing at 3000 kg.	Weight after carburizing	Weight after N_2 atmosphere heating at 1850°F for 1/2 hour
A.	0.80732	0.80885	0.80732
B.	0.17165	0.17208	0.17191
C.	0.16547	0.16593	0.16578

	Percentage Weight Increase after Carburizing	Percentage Weight Increase after homogenization	Estimated Percentage Carbon
A.	0.17	0	0.07
B.	0.25	0.15	0.26
C.	0.27	0.19	0.29

TABLE II

Sample No.	Pressing Pressure (psi)	Carburizing Temperature °C	Time (Hours)	Percentage Weight Increase
Carbonyl Iron "L"				
1	23,000	925	0.34	5.55
2	23,000	925	0.34	5.82
3	23,000	925	0.50	6.20
4	23,000	925	0.50	6.45
5	9,000	925	0.50	7.50
6	138,000	925	22.5	3.00
7	138,000	925	22.5	3.18
8	23,000	925	22.5	10.4
9	23,000	925	22.5	12.0
10	9,000	925	22.5	15.3
11	9,000	925	22.5	14.6
12	138,000	850	23.0	2.07
13	138,000	850	23.0	2.40
14	138,000	850	23.0	2.30
15	138,000	850	23.0	2.80
16	69,000	850	23.0	3.80
17	69,000	850	23.0	3.62
18	138,000	660	25.8	2.70
19	138,000	660	25.8	2.71
20	46,000	660	25.8	6.12
21	46,000	660	25.8	6.12
22	138,000	650	35.8	3.19
23	138,000	650	35.8	3.28
24	46,000	650	35.8	6.36
25	46,000	650	35.8	6.34
26	138,000	595	41.0	0.69
27	138,000	595	41.0	0.68
28	138,000	585	16	0.10
29	138,000	585	16	0.07

TABLE II (continued)

Sample No.	Pressing Pressure (psi)	Carburizing Temperature °C	Time (Hours)	Percentage Weight Increase
Electrolytic Iron (As Plated-Thin Sheet)				
Analysis (C 0.006%, Mn < 0.001%, S 0.006%, Si 0.002%, P < 0.002%)				
30	-	925	22.5	3.56
31	-	925	22.5	3.14
32	-	925	22.5	3.40
33	-	925	22.5	2.36
Ingot Iron (Thin Piece)				
Analysis (C 0.010%, Mn 0.013%, S 0.022%, Si 0.001%, P 0.005%)				
34	-	925	22.5	4.80
Tungsten Powder				
35	46,000	995	21.0	4.07
36	46,000	995	21.0	4.19
Titanium Powder				
37	46,000	995	21.0	23.0
38	46,000	995	21.0	22.3

It may be noted that the larger compact, more loosely pressed because of lack of hydrostatic conditions in the powder mass, showed little permanent gain in carbon because of the greater quantities of oxygen absorbed along with the carbon. Samples 28 and 29 of Table II also showed no permanent weight gains. Yet after carburizing the presence of carbide was ascertained by microscopic examination.

In contrast with shorter times and lower temperatures are the results at somewhat higher temperatures and especially at longer times. Sample No. 19 of Table II when heated at 1040°C showed no greater weight loss than experienced with the samples homogonized for isothermal transformation studies and also gave a microstructure of cementite and pearlite.

In Table II a number of values are shown of carbon contents in a range of 5-15%. It appears that the carbon is first picked up in solution in the gamma ferrite at higher temperatures, then precipitated as Fe_3C which then decomposes to give graphite. At lower temperatures, say 650°C, the carbide appears to be stable even in contents of 6.35% carbon. Incidentally this material, as one would expect, is very hard and cuts glass readily.

At this time it might be of interest to show what happens, using energized charcoal, below the temperatures listed in Table II. The following data listed in Table III were obtained:

TABLE III

Sample No.	Pressing Pressure (psi)	Carburizing Temperature °C	Time (Hours)	Percentage Weight Increase
		Carbonyl Iron "L"		
1	138,000	540	60	1.43
2	138,000	540	60	1.43
3	138,000	540	60	1.35
4	138,000	540	60	1.53
5	46,000	540	60	7.03
6	46,000	540	60	7.05
7	46,000	540	60	6.75
8	46,000	540	60	6.85
9	23,000	540	60	10.27
10	23,000	540	60	10.37

Samples 2, 3, 5 and 6 were analyzed for carbon chemically and showed none. Further sample No. 4 after being heated at 1040°C for 1 1/2 hours showed a weight loss of but 0.00008 grams. Microscopic examination revealed no carbon, but instead showed iron oxide dispersed in a matrix of alpha ferrite. It is quite obvious that oxidation has taken place preferentially. From experiments performed it appears that oxidation occurs definitely under the pack carburizing conditions maintained when the temperature is 565°C and carburization occurs definitely at 585°C. These values hold when Na_2CO_3 energizer is used. When ordinary hardwood charcoal (on 200 through 150 mesh) without energizer intentionally added is used, then even at 650°C there is no carburization but instead oxidation occurs.

In Table IV are summarized the equilibrium constants for a series of reactions and in Figure 42 is a plot of data for reactions (2) and (4). Data for (4) is given at 0.2 and 1 atmosphere pressure. From this data one might well expect results such as have been obtained. It shows that a temperature would be expected at which oxidation occurs preferentially. Not enough information, unfortunately, exists to ascertain whether the introduction of the energizer shifts the CO concentration or whether it serves to shift the pressure of CO + CO_2 to a lower value. As a result no explanation is offered for the fact that oxidation occurs even at 650°C when no Na_2CO_3 energizer is used. See Figure 47. It might also be remembered that the constants for equation (4) are for carbon as graphite and not amorphous carbon.

One experiment conducted on Carbonyl Iron "L" showed that in sixteen hours at 925°C a carbon content of 1.20% was reached in ordinary hardwood charcoal while under the same conditions of time and temperature but 0.69% C resulted in using pure finely divided graphite. This too may be a condition of rate of absorption rather than CO concentration maintained. Along these same lines differences were apparent in using charcoal of varying mesh. For example, carbonyl iron "L" was carburized 51 hours at 925°C in 5-8 mesh charcoal (no energizer) and another set of samples were carburized in 200 mesh charcoal (no energizer other than the ash of the

TABLE IV

See Bibliography (21)

Equilibrium Constants for Reactions 1 to 5[a]

t°C	t°F	$K_1 = \frac{P_{H_2}}{P_{H_2O}}$	$K_2 = \frac{P_{CO}}{P_{CO_2}}$	$K_3 = \frac{P_{H_2} \times P_{CO_2}}{P_{H_2O} \times P_{CO}}$	$K_4 = \frac{P^2_{CO}}{P_{CO_2}}$	$K_5 = \frac{P^2_{H_2}}{P_{CH_4}}$
400	752	9.12*	0.74*	12.3	9×10^{-5}	5.66×10^{-2}
450	842	6.38*	0.86*	7.38	7.3×10^{-4}	0.164
500	932	4.68*	0.96*	4.88	4.7×10^{-3}	0.422
550	1022	3.53*	1.03*	3.45	0.023	0.977
600	1112	2.99	1.17	2.55	0.096	2.09
650	1202	2.65	1.35	1.96	0.343	3.92
700	1292	2.38	1.53	1.56	1.06	7.16
750	1382	2.17	1.72	1.27	2.96	12.3
800	1472	2.00	1.90	1.05	7.48	20.1
850	1562	1.84	2.07	0.891	17.46	31.8
900	1652	1.72	2.24	0.765	37.76	48.3
950	1742	1.61	2.41	0.668	76.70	71.0
1000	1832	1.51	2.57	0.589	146.5	102.4
1050	1922	1.44	2.72	0.527	264.0	141.2
1100	2012	1.37	2.88	0.474	463.4	192.0
1150	2102	1.31	3.03	0.433	767.4	256.0
1200	2192	1.26	3.21	0.395	1244	335.0
1250	2282	1.22	3.36	0.363	1945	431.5
1300	2372	1.18	3.49	0.339	2951	547.0

*Stable oxide at this temperature is Fe_3O_4 not FeO; the equilibrium constants so marked are not so accurate as the others.

[a] (1) $Fe + H_2O = FeO + H_2$
(2) $Fe + CO_2 = FeO + CO$
(3) $CO + H_2O = CO_2 + H_2$
(4) $C + CO_2 = 2\ CO$
(5) $CH_4 = C + 2\ H_2$

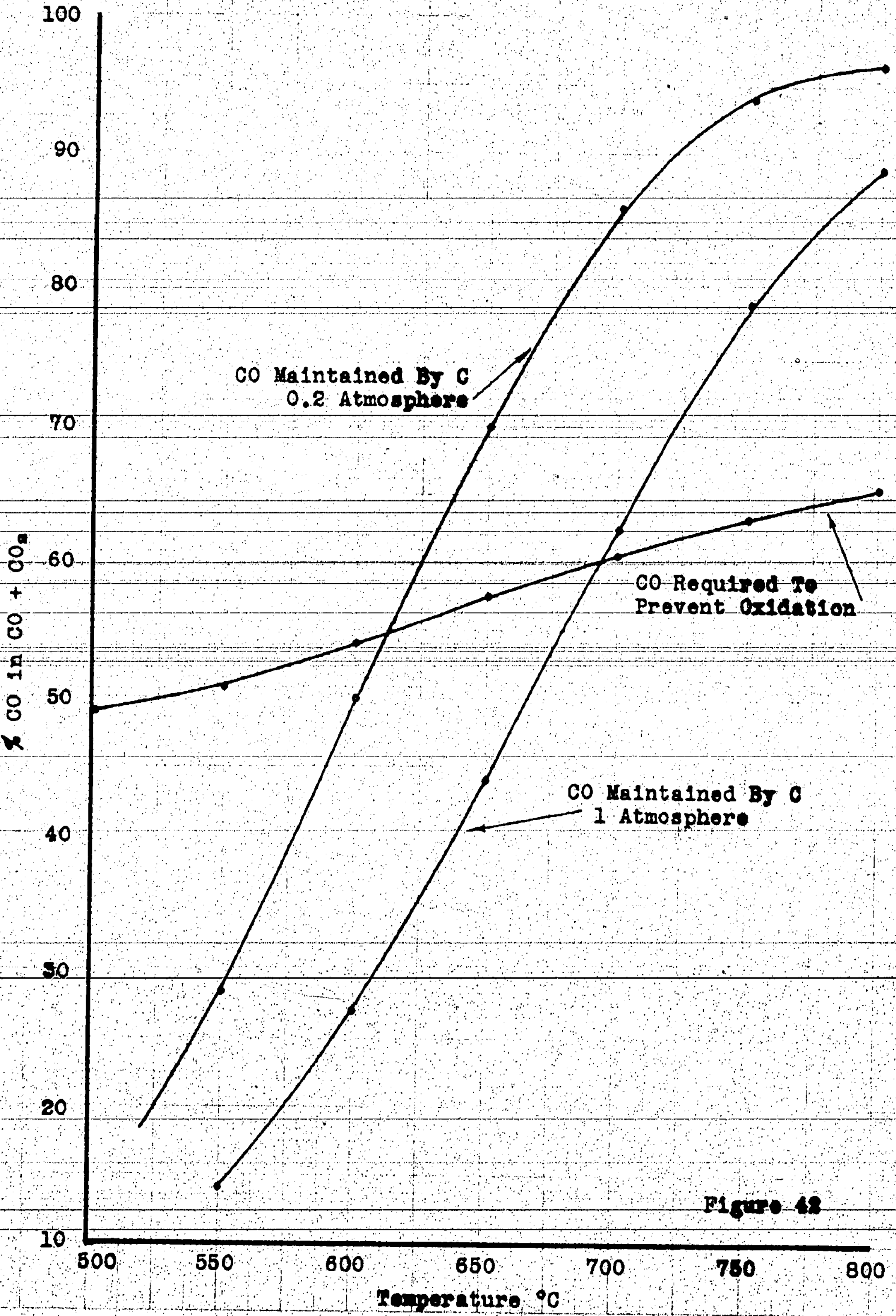

100
90
80
70
60
50
40
30
20
10
% CO in CO + CO_2
500
550
600
650
700
750
800
Temperature °C
CO Maintained By C
0.2 Atmosphere
CO Required To
Prevent Oxidation
CO Maintained By C
1 Atmosphere

Figure 42

charcoal). The coarse charcoal run yielded samples of 0.95% C while the fine material gave 1.20% C. Again it is difficult to draw conclusions.

Microscopic studies revealed a number of interesting structures resulting from these carburizing studies. These are shown in Figures 43-50.

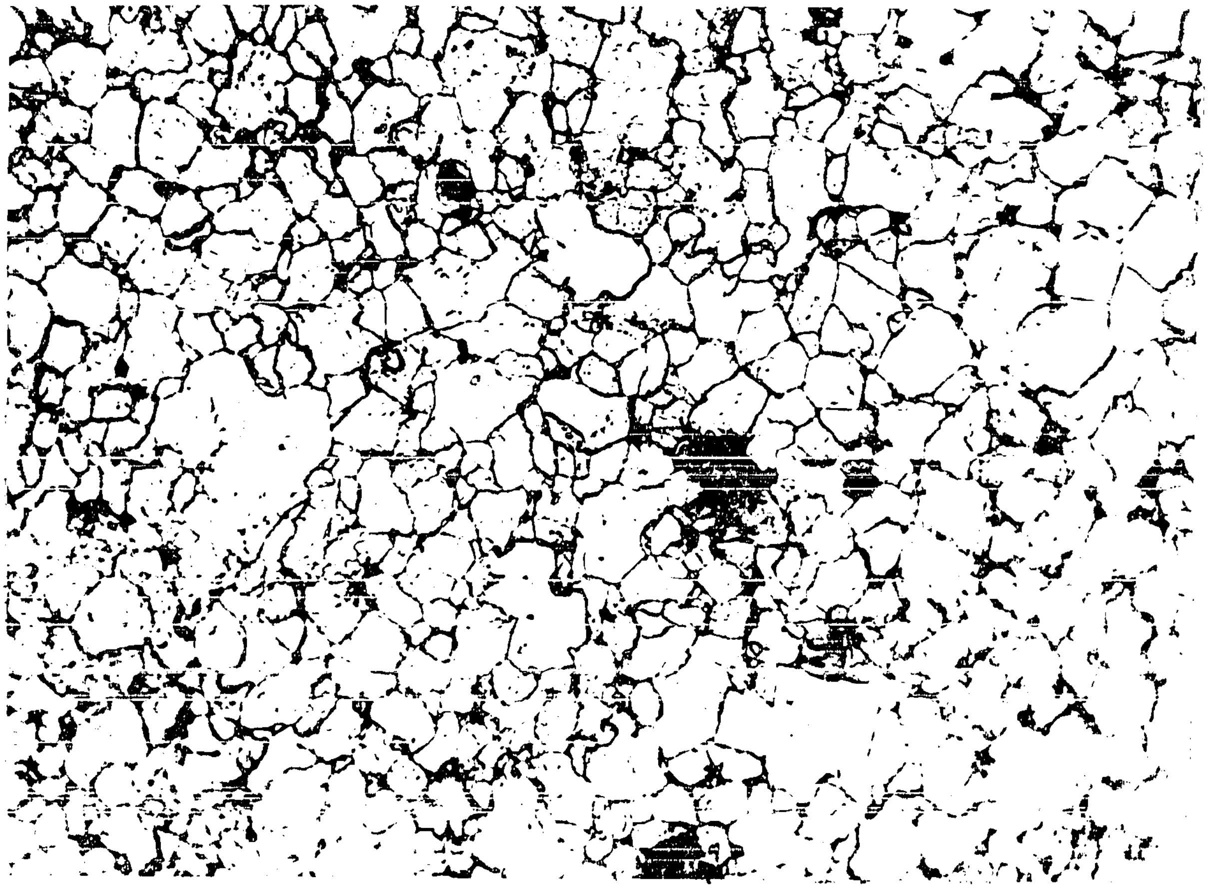


Figure 43
Sample No. 29 Table II
Laboratory No. 40

Alpha Ferrite and Cementite

Carburized at 585°C for 16 hours in Na_2CO_3 energized hardwood charcoal.

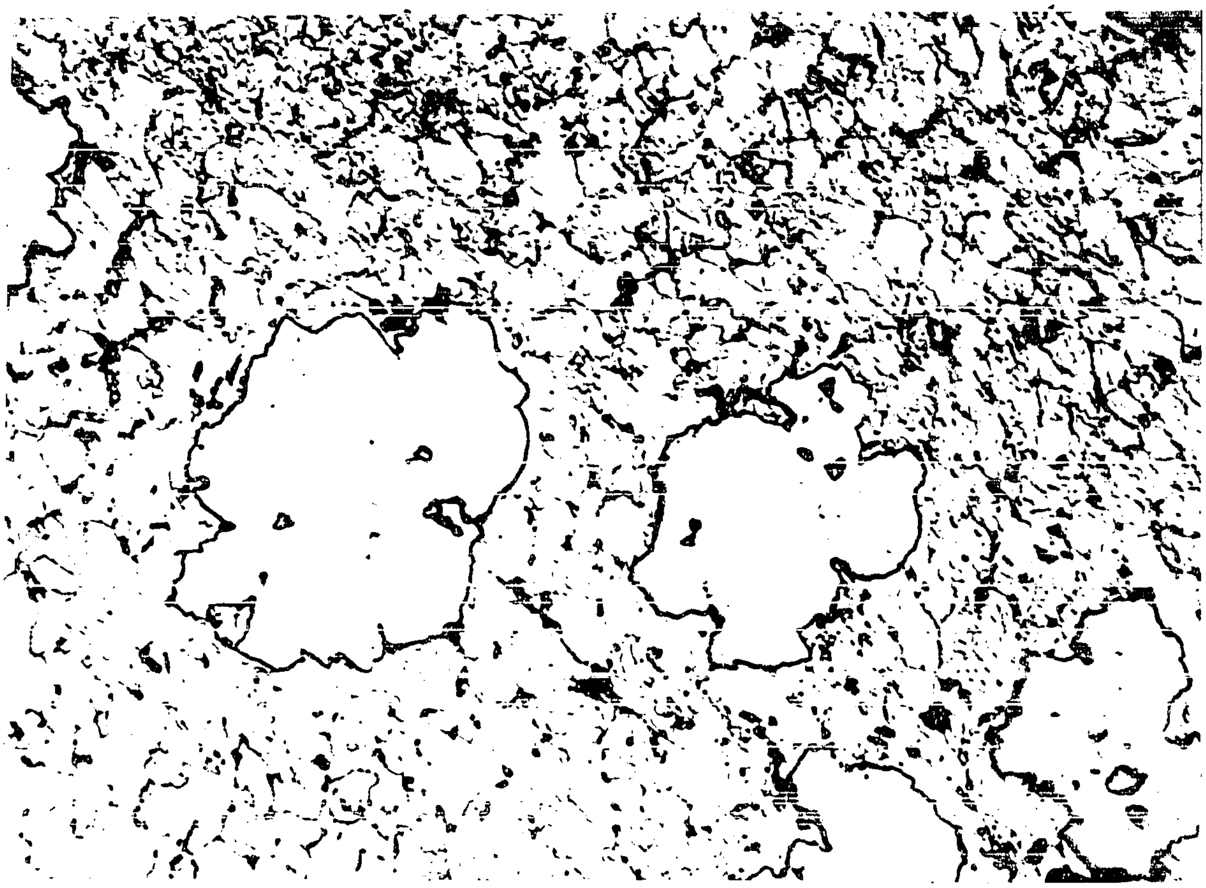


Figure 44
Sample No. 26 Table II
Laboratory No. 25

Alpha Ferrite and Cementite

Carburized at 595°C for 41 hours in Na_2CO_3 energized hardwood charcoal.

Figure 45
Sample No. 4 Table III
Laboratory Sample No. 43

Iron Oxide and Alpha Ferrite

"Carburized" at 540°C for 60 hours in Na_2CO_3 energized hardwood charcoal, then heated to 1040°C for 1 1/2 hours in nitrogen atmosphere.

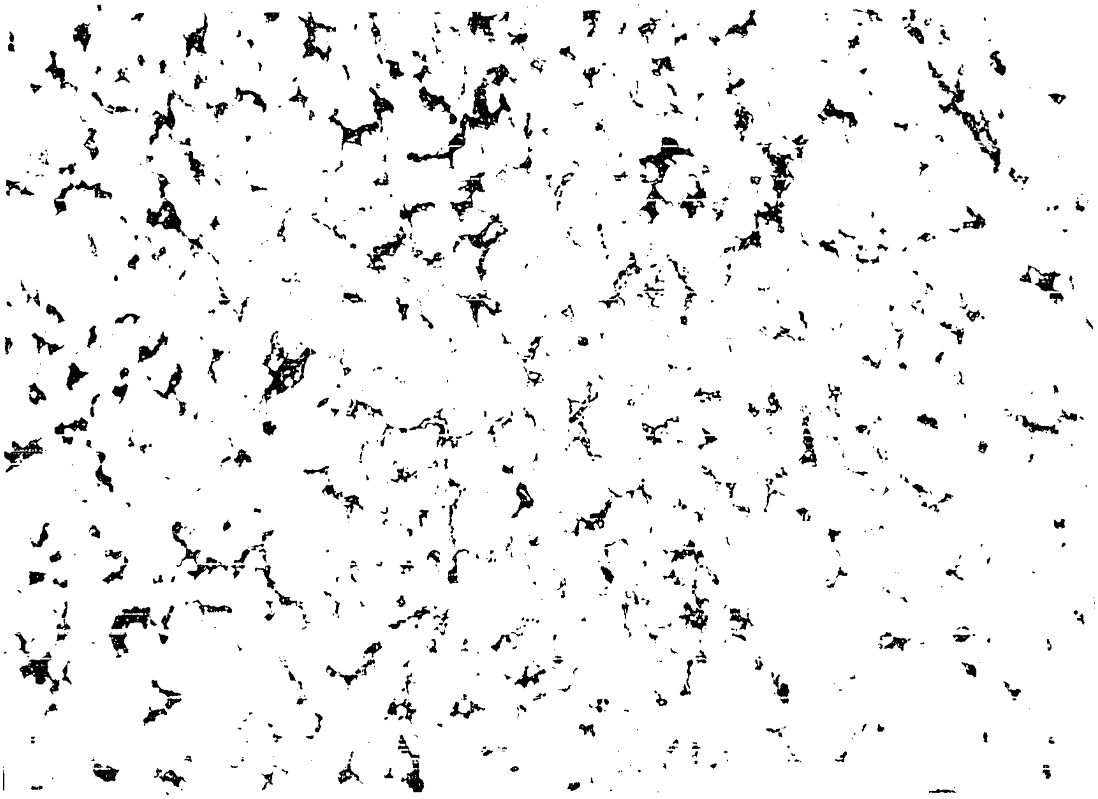


Figure 46
Sample No. 1 Table III
Laboratory No. 31a

Iron Oxide and Alpha Ferrite

"Carburized" at 540°C for 60 hours in Na_2CO_3 energized hardwood charcoal.

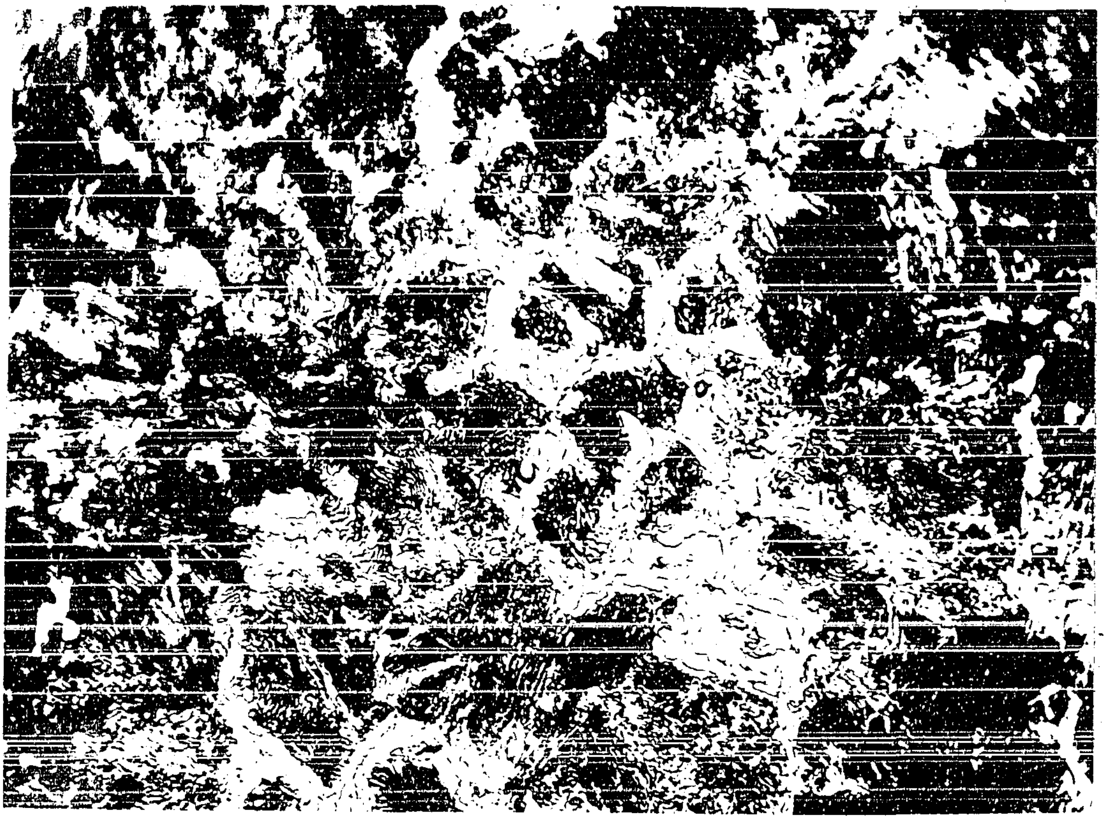


Figure 46a.
Sample No. 19 Table II
Laboratory No. 42

Cementite and Pearlite

Carburized at 660°C for 25.8 hours in Na_2CO_3 energized hardwood charcoal and then austenitized at 1040°C for thirty minutes and allowed to cool.

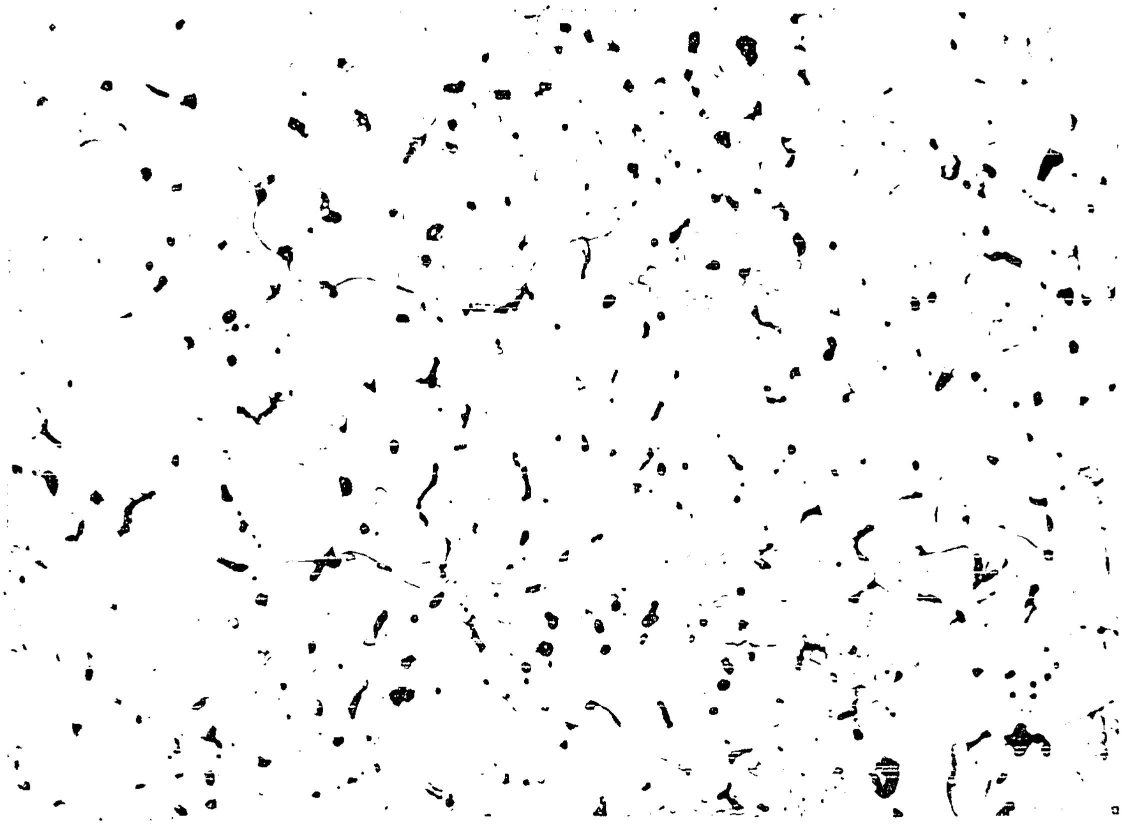


Figure 47
Laboratory No. 23

Iron Oxide and Alpha Ferrite

"Carburized" at 650°C for 16 hours in hardwood charcoal without Na_2CO_3 energizer added, then the sample was heated to 1000°C for thirty minutes in the nitrogen atmosphere.

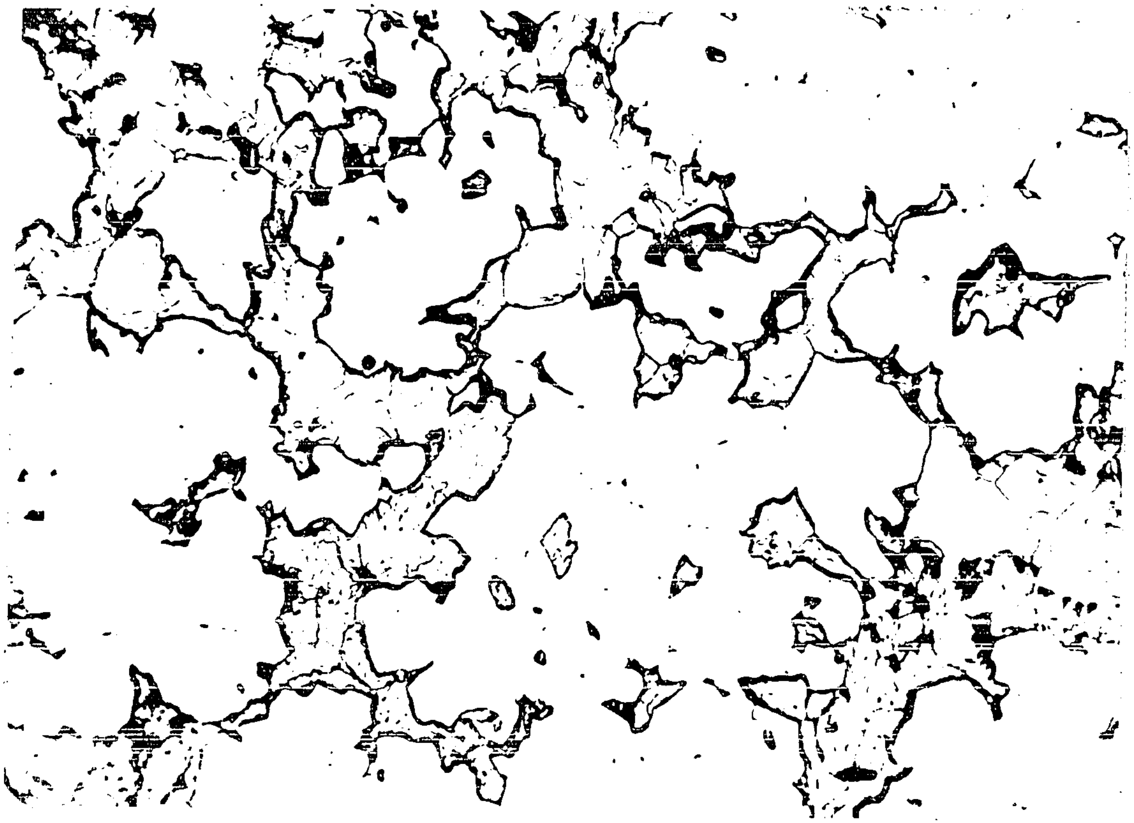


Figure 48
Sample No. 22 Table II
Laboratory No. 18

Cementite and Alpha Ferrite

Carburized at 650°C for 35.8 hours in Na_2CO_3 energized hardwood charcoal.

Figure 49
Sample No. 31 Table II
Laboratory No. 76

Cementite and Pearlite

Electrolytic Iron carburized at 925°C for 22 1/2 hours in Na_2CO_3 energized hardwood charcoal.

Figure 50
Sample No. 34 Table II
Laboratory No. 78

Cementite and Pearlite

Ingot Iron carburized at 925°C for 22 1/2 hours in Na_2CO_3 energized hardwood charcoal.

Carburizing Studies in Hardwood Charcoal

In addition to studies on energized charcoal some data were obtained on carbon absorption rates in ordinary hardwood charcoal. Figure 51 shows the results for carburizing 0.2 g samples of carbonyl iron "L" at 925°C. The samples were pressed at 138,000 psi. The value of 1.22 percentage weight increase for 3000 minutes is equivalent to about 1.29% C. Figure 52 illustrates the differences caused by a variation in pressing pressures used for compacting the carbonyl iron "L" over relatively short time carburizing periods. For lower pressing pressures there is a much more rapid weight gain. This is caused by oxidation combined with subsequent carburization and as a result the curve goes through a maximum. At the higher pressing pressures no maximum is evident because the oxidation rate is decreased by the more compact powder. Because of the oxidation possible in pack carburizing as the mass is being heated it would seem much more practicable normally to use gas carburizing procedures where the compressed powder samples are introduced into the hot zone without a great temperature lag. If long time carburizing is not objectionable, as was the case in samples prepared for the austenite decomposition studies, the pack carburizing procedure is excellent for preparation of pure steel of controlled carbon content. It was easier with limited facilities to prepare pure steels of controlled carbon content by this method

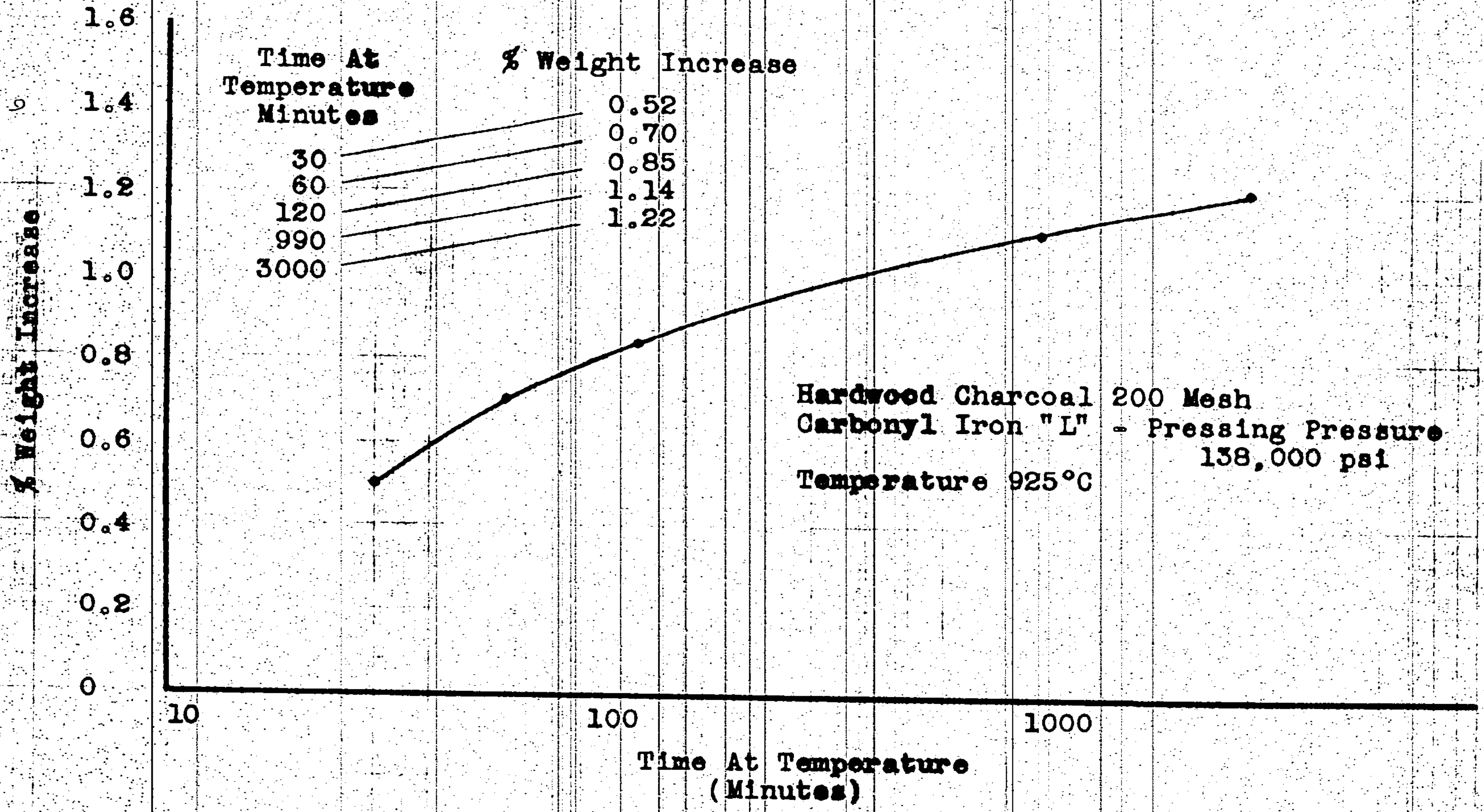

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
% Weight Increase
10
100
1000
Time At Temperature
(Minutes)
Time At Temperature Minutes
% Weight Increase
30 0.52
60 0.70
120 0.85
990 1.14
3000 1.22
Hardwood Charcoal 200 Mesh
Carbonyl Iron "L" - Pressing Pressure 138,000 psi
Temperature 925°C

Figure 51

than by gas carburizing or by mixing graphite and iron followed by subsequent heating to form austenite.

In twenty and 140 minutes at temperature under conditions shown in Figure 52 the percentage weight increase varied with pressing pressure as shown in Table V.

TABLE V

Pressing Pressure (psi)	Percentage Weight Increase
23,000	1.61
46,000	1.38
69,000	1.27
92,000	1.15
115,000	0.96
138,000	0.80

Time at 925°C was 20 minutes

Pressing Pressure (psi)	Percentage Weight Increase
23,000	1.05
46,000	1.06
69,000	1.02
92,000	1.03
115,000	1.01
138,000	0.96

Time at 925°C was 140 minutes

In comparing Figures 51 and 52 one may at first thought believe that they are in conflict. In thirty minutes at temperature the weight increase shown in Figure 51 is 0.52% while in Figure 52 it is given as 0.84%. These values are not in conflict when one considers that in the coarser charcoal the 0.84% weight increase is actually due to a greater quantity of oxide whereas the 0.52% weight change is more nearly the actual carbon content.

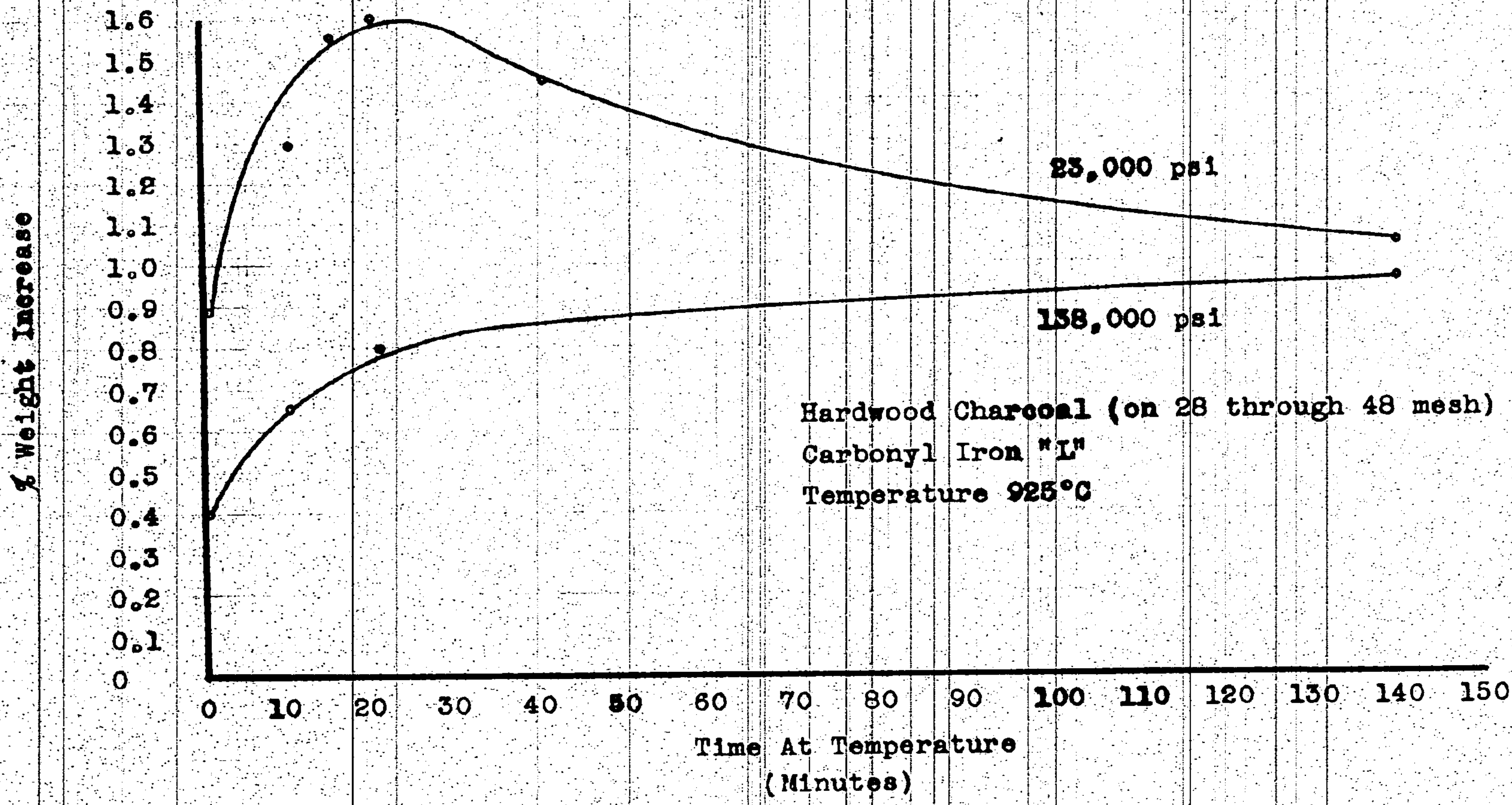

% Weight Increase
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
23,000 psi
138,000 psi
Hardwood Charcoal (on 28 through 48 mesh)
Carbonyl Iron "L"
Temperature 925°C
Time At Temperature
(Minutes)

Figure 52

Maximum Carbon Content of Carburized Cases

Some investigators believe that the maximum carbon content of carburized cases is limited by the Ac_{cm} temperature in the iron-iron carbide constitutional diagram when the carbon monoxide content is sufficient to permit going to that high a carbon content. Recently consideration has been given to this problem by Floyd E. Harris (22) and Sidney Breitbart (23).

Most certainly this is not the case when Na_2CO_3 energizer is used, as has been shown, but when it is not intentionally used there might be some question. Many samples carburized at 925°C in hardwood charcoal show that after long times (60 hours) on lightly pressed samples the carbon content is 1.3% at most. The value usually given for the Ac_{cm} at 925°C is about 0.1% less. At 1065°C values as high as 2.3% were obtained after forty hours at the carburizing temperature. The Ac_{cm} given at 1065°C is close to 1.55% C. At 800°C in hardwood charcoal (on 200 through 150 mesh) the following carbon contents were reached:

Pressing Pressure (psi)	Percentage Carbon
138,000	0.90
138,000	0.91
46,000	0.90
46,000	0.90
23,000	0.90
23,000	0.91

At 800°C equilibrium data shows that the Ac_{cm} value would not be reached. The carbon content would be limited to about 0.65% C. The data at 800°C shows that the less dense compacts do not reach unusually high carbon contents.

Perhaps not enough data are available, but there seems to be no definite theoretical reason why the carbon content should be limited to the Ac_{cm} temperature. It would seem more logical to expect precipitation of Fe_3C as a second phase.

Carburizing of Electrolytic and Hydrogen Reduced Iron Powders

Electrolytic iron powder and hydrogen reduced iron powder of the following analyses were given a hydrogen treatment at 260°C for twenty four hours. This treatment was similar to the one given the carbonyl iron "L" used for all other studies.

Electrolytic Iron (annealed)

Total Iron	99.50%
Copper	0.01
Silica	0.02
Manganese	0.027
Zinc	0.090
Nickel	None
Sulphur	0.001
Phosphorus	0.002
Free Carbon	0.005
Oxygen	-

Hydrogen Reduced Iron Powder

Total Iron	99% minimum
Carbon	0.04
Manganese	0.18

After the hydrogen treatment these powders were pressed and carburized along with carbonyl iron "L". Weight changes were

Pressing Pressure	138,000 psi
Carburizing temperature	1500°F
Time	22 hours
Carburizing Medium	Hardwood Charcoal

	Percentage Weight Change
Carbonyl Iron "L"	0.77%
Electrolytic Iron	0.52%
Hydrogen Reduced Iron	0.93% Loss

It was quite evident that the loss in weight encountered was with the hydrogen reduced iron caused by the presence of the oxide in the powder. Microstructures prepared of all of them showed eutectoid carbon content. A fair estimate is that all were about 0.85% carbon. In an endeavor to gain some concept of the oxygen contents of these various powders they were run in compressed form (46,000 psi) at 2000°F. The loss in hydrogen (not necessarily all oxygen) after twenty five hours was

Carbonyl Iron "L"	0.04%
Electrolytic Iron	0.70%
Hydrogen Reduced Iron	1.92%

The time of twenty five hours was split into three periods to determine that a constant weight had been reached. The percentage losses varied with time as follows:

	Hydrogen Loss		
	After 11 1/2 hours	After 15 hours	After 25 hours
Carbonyl iron "L"	0.04	0.04	0.04
Electrolytic Iron	0.56	0.70	0.70
Hydrogen Reduced Iron	1.88	1.92	1.92

This indicates that under these conditions the oxygen removal is slower with the electrolytic iron than with the hydrogen reduced iron, which has a greater oxygen content. This is also evident when one compares the losses in hydrogen and the percentage weight changes. By adding these values algebraically and considering that the 0.04% carbon in the hydrogen reduced iron is lost during the hydrogen treatment and present in the original powder the percentage weight changes in the previous carburizing experiment should have been:

Carbonyl Iron "L"	+ 0.81%
Electrolytic Iron	+ 0.15%
Hydrogen Reduced Iron	- 1.07%

instead of

Carbonyl Iron "L"	+ 0.77%
Electrolytic Iron	+ 0.52%
Hydrogen Reduced Iron	- 0.93%

The above calculations are made assuming the actual carbon content of the compact to be 0.85%. The significant point is that 0.37% oxygen remains in the electrolytic iron powder compacts as compared to 0.14% in the hydrogen reduced powder compacts.

Another set of all three type irons were carburized for thirty six hours at 815°C in hardwood charcoal (on 150 through 100 mesh). The samples were pressed at 138,000 psi. After carburizing the compacts were homogenized at 1100°C for fifty five minutes in the nitrogen atmosphere. Results were as follows:

	Weight Percentage Gain As Carburized	Weight Percentage Loss in Homogenization
Carbonyl Iron "L"	0.75	0.06
Electrolytic Iron	0.32	0.39
Hydrogen Reduced Iron	- 1.05	0.23

These results confirm what has been stated previously, namely that in spite of higher oxygen content initally present in the hydrogen reduced powder, more of the oxide is reduced in carburizing. This is true for the conditions under which these experiments were performed, and may not be general. This fact, if generally true, would be of marked importance in any steels made by carburizing methods because if they were to be heat treated they would decarburize when austenitized. This, of course, would result in poor control of the properties of the product.

When samples of all three type powders were compacted at 46,000 psi, reduced in hydrogen for twenty five hours at 1100°C, then carburized at 815°C for thirty six hours in hardwood charcoal (on 150 through 100 mesh) they gave weight percentage increases of

Carbonyl Iron "L"	0.76%
Electrolytic Iron	0.78
Hydrogen Reduced Iron	0.78

These might be considered essentially the same. This is but a limited amount of work along these lines but nevertheless indicates a definite trend.

CONCLUSIONS

The more important conclusions reached in making this study are that:

1. Very pure steels may be prepared by pack carburizing a high purity iron such as carbonyl iron "L".

2. Pure steels made from powder without going into the liquid state have austenite transformation characteristics which do not differ markedly from those found in comparable steels made by utilization of the liquid phase. This is considered by the author a significant contribution toward establishing the thesis that by either method products may be produced, without too much difficulty, that are equivalent with respect to composition and grain structure.

3. Sodium carbonate used as an energizer alters markedly the quantity of carbon absorbed in carburizing carbonyl iron "L" compacts.

4. Carbon absorption may take place with sodium carbonate energized hardwood charcoal at temperatures as low as 585°C.

5. The oxide content of iron powders is an important factor to consider in the preparation of steels by carburization, particularly those which may be subjected to heat treatment to gain high strengths.

Since it was possible to produce a high grade steel it would seem relatively simple, in further work, to study the influence of the introduction of even small quantities of other elements and compounds into the powder compacts. With a high purity product it may be possible to show, for example, whether cobalt actually does increase the rate of austenite decomposition in steels and what the mechanism may be. To illustrate further, a more careful grain growth study could be conducted on steels to show more precisely the influence of various compounds such as aluminum oxide on grain growth phenomena. An opportunity exists immediately for securing data to learn how energizers function in carburizing iron and steel. This study might well begin by employing other compounds as energizers. Uncovering some of the secrets in nature is always difficult but it is sincerely believed that with respect to the metallic state the job may be made much easier through use of metal powders.

BIBLIOGRAPHY

(1) Jones, W. D., "Principles of Powder Metallurgy", Edward Arnold and Company, London, England, 1939, p.77.

(2) Wulff, John, "Powder Metallurgy" Society for Metals, Cleveland, Ohio, 1942.

(3) Baëza, W. J., "A Course in Powder Metallurgy", Reinhold Publishing Corporation, New York, New York, 1943.

(4) Skaupy, Franz, "Principles of Powder Metallurgy", Philosophical Library, New York, New York, 1944.

(5) A.S.T.M. "Symposium on Powder Metallurgy", American Society for Testing Materials, Philadelphia, Pennsylvania, 1943.

(6) A.I.M.E. "Conference on Production and Design Limitations and Possibilities for Powder Metallurgy Parts", American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, Vol. 161, 1945, p. 524-634.

(7) McDonald, N. B., "Powdered Metals - A Bibliography", The Library of Congress, Division of Bibliographies: No. 2, Washington, D.C., 1943.

(8) Carpenter, Clark B., "Powder Metallurgy - A Review of its Literature", Colorado School of Mines Quarterly, Volume 36, No. 4, 1941.

(9) Institute of Metals, "Metallurgical Abstracts" Powder Metallurgy Sections, Vols. VI-XI, (1939-1944) Institute of Metals, London, England.

(10) A.S.M. "Review of Metal Literature", Powder Metallurgy Sections, Vols. I and II (1944 and 1945) American Society for Metals, Cleveland, Ohio.

(11) Schumacher, E. E. and Souden, A. G., "Powder Metallurgy", Metals and Alloys, Vol. 20, 1944, p. 1327-1339.

(12) Peters, F. P., "Design Factors for the Metal Forms with which Powder Metallurgy May Compete", Transactions of the American Institute of Mining and Metallurgical Engineers, Vol. 161, 1945, p. 527-530.

(13) Langhammer, A. J., "Powder Metallurgy as Applied to Machine Parts", Transactions of the American Institute of Mining and Metallurgical Engineers, Vol. 161, 1945, p. 531-535.

(14) Balke, C. W., "The Effect of Pressure on the Properties of Compacts", Symposium on Powder Metallurgy, American Society for Testing Materials, Philadelphia, Pennsylvania.

(15) Wulff, John, "Alloy Steels from Powders", Powder Metallurgy, American Society for Metals, Cleveland, Ohio, 1942.

(16) Lenel, F. V., "Oil Pump Gears", Powder Metallurgy, American Society for Metals, Cleveland, Ohio, 1942.

(17) Margolies, A. S., "Carbursintering of Iron Powders", The Iron Age, Vol. 157, No. 9, 1946, p. 60-63.

(18) Stansbury, E. E., "A Study of Several Variables Affecting the Rate of Martensite Formation", University of Cincinnati Thesis, 1946.

(19) Greninger, A. B., The Martensite Thermal Arrest in Iron-Carbon Alloys and Plain Carbon Steels, Transactions of the American Society for Metals, Vol. XXX, 1942, p. 1-26.

(20) Zener, C., "Kinetics of the Decomposition of Austenite", Metals Technology, Vol. 13, No. 1, T.P. 1925, January, 1946.

(21) Austin, J. B. and Day, M. J., "Chemical Equilibrium as a Guide in the Control of Furnace Atmospheres - A Review of Equilibrium Data", Controlled Atmospheres, American Society for Metals, Cleveland, Ohio, 1942.

(22) Harris, Floyd E., "Maximum Carbon in Carburized Cases", Metal Progress, Vol. 45, 1944, p. 683-686.

(23) Breitbart, Sidney, "Maximum Carbon in Carburized Cases", Metal Progress, Vol. 47, 1945, p. 1121-1127.