

DEC 2 1974

*Reprinted from*

**Transactions of The Iron and Steel Institute of Japan**

*M. Fujita*

**The Iron and Steel Institute of Japan  
Keidanren Kaikan (3rd Floor)  
9-4, Otemachi 1-chome, Chiyoda-ku, Tokyo  
100, Japan**

# The Effect of High Pressure on the Isothermal Transformation in High Purity Fe-C Alloys and Commercial Steels\*

By Mitsutane FUJITA\*\* and Masatoshi SUZUKI\*\*

## Synopsis

The effects of high pressure on the isothermal transformation were investigated for three kinds of high purity Fe-C alloys and commercial steels which had corresponding carbon contents to the alloys. The experiments were carried out at 29 or 38.5 kbar using a "girdle" type high pressure apparatus, and the transformation behaviours of these alloys and steels were examined.

The results obtained were as follows;

The rates of isothermal transformation both in Fe-C alloys and commercial steels were retarded by an increase of pressure. This retardation was much larger in the Commercial steels. By increasing the pressure from 29 to 38.5 kbar, the incubation time increased by approximately five times for all alloys and steels. The structures obtained in the isothermal transformation at high pressure and at relatively higher temperatures could be explained from the phase equilibrium diagram under high pressure which showed some changes from that at atmospheric pressure. At relatively lower temperatures, singular structures so-called "aggregate" or "columnar bainite" were observed as a result of high pressure isothermal transformation, in place of acicular bainite in the case of atmospheric pressure. The temperature ranges in which these structures appeared were also determined. Furthermore, in the case of a commercial steel containing 1.1% C, it was observed that the shape of carbides always changed from spherical to acicular with an increase of pressure from 29 to 38.5 kbar.

## 1. Introduction

It is known that the pressure, one of the thermodynamic variables, affects the phase equilibrium and the kinetics of transformation in metals and alloys; for example, a hcp( $\epsilon$ ) structure in pure iron and iron alloys is observed even at the room temperature in high pressure treatment.<sup>1-4)</sup>

The transformation behaviour of austenite to pearlite, bainite and martensite in steels has been studied extensively at atmospheric pressure. On the other hand, there are some papers<sup>5-7)</sup> discussing the effects of pressure on the decomposition of austenite, in which it is described that the decomposition was retarded with an increase of pressure.

Radcliffe *et al.*<sup>5)</sup> examined the isothermal transformation of austenite at 42 kbar for high purity Fe-C alloys containing 0.08 to 1.23% C, and reported that the irregular ferrite-carbide "aggregates" appeared in the temperature range in which the formation of bainitic structure would be expected at atmospheric pressure, and that no acicular bainite could be observed even at the pressure as decreased as 15 kbar. Nilan<sup>6)</sup> found the other singular structure, which he named as "columnar bainite", at 24 and 30 kbar in the temperature range in which acicular bainite would be originally observed in plain carbon steel at atmospheric pressure. The differences in the appearance of structure between them are thought to be due to

the differences in their experimental condition such as pressure range, experimental apparatus and chemical composition of materials. Hilliard and Cahn<sup>7)</sup> determined the growth rate of pearlite in high purity Fe-C alloys and commercial steels at 34 kbar, and reported that the retardation on the growth of pearlite by pressure was far greater in the latter and also that those activation volumes for the diffusion of carbon which controls the growth rate of pearlite was considerably larger in commercial steels. These results both indicate that the effect of pressure on this reaction is more outstanding in commercial steels than in Fe-C alloys. Therefore, it is supposed that if the same effect as described above is brought on the bainite reaction, the changes of structure in commercial steels at high pressure would be expected to show some difference to the one in Fe-C alloys.

Tanaka<sup>8)</sup> reviewed the phase equilibria in Fe-C system at atmospheric pressure in detail, and suggested the decomposition behaviour of austenite. On the other hand, under high pressure, the phase equilibria near the eutectoid point was reported by some researchers,<sup>5,7,9,10)</sup> and those results showed that the eutectoid point tended to shift to lower temperature and that the composition of carbon at that point decreased with an increase of pressure.

Figure 1 is composed of the phase diagram<sup>10)</sup> and Ms point<sup>11)</sup> at atmospheric and high pressure on Fe-C alloys which were decided experimentally or calculated from thermodynamic data.

The purpose of the present study is in the effects of high pressure on the isothermal transformation be-

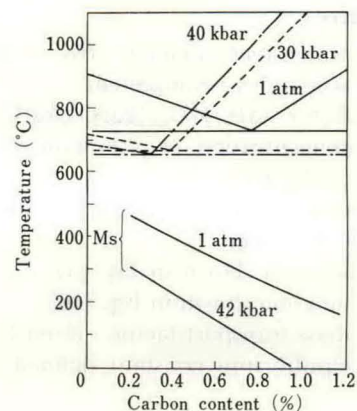


Fig. 1. Effect of pressure on phase equilibria<sup>10)</sup> and Ms<sup>11)</sup> temperature in the Fe-C system. These were determined experimentally and calculated from thermodynamic data respectively

\* Originally published in *Tetsu-to-Hagane*, 57 (1971), 1676, in Japanese. English version received July 28, 1973.

\*\* National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153.

haviour of high purity Fe-C alloys and commercial steels. Special emphasis is placed on the determination of TTT diagrams and on the observation of structure changes caused by pressure. In addition, the behaviour of carbides which appeared during isothermal transformation is also discussed.

## II. Experimentals

### 1. Materials

The materials used in this study were three high purity Fe-C alloys containing 0.28, 0.42 and 0.99% C respectively, and three commercial steels (JIS S20C, S50C, and SK3) having nearly the corresponding carbon contents to those of the alloys. The chemical composition of them are shown in Table 1. On the basis of the phase equilibria of Fe-C system under high pressure shown in Fig. 1, the carbon content in these materials was chosen so as to obtain the following at 1 atm, and at 29 and 38.5 kbar:

(1) Showing a hypoeutectoid structure at 1 atm, but a nearly eutectoid structure is expected under high pressure. (A-2, S20C)

(2) Showing a hypoeutectoid structure at 1 atm, but a hypereutectoid structure is expected under high pressure. (A-4, S50C)

(3) Showing hypereutectoid structures regardless of the change of pressure. (A-9, SK3)

The Fe-C alloys were melted in a high frequency vacuum furnace with the electrolytic iron and a Fe-C mother alloy (5% C) which had been prepared beforehand, and cast to 6 kg ingots. These ingots were heat treated and hot and cold worked to 3 mm $\phi$  rods by rolling, swaging and drawing. The commercial steel bars of 40 mm $\phi$  were also finished to 3 mm $\phi$  rods in the same manner as that of the alloys. These rods were normalized in a vacuum furnace and used to the high pressure experiments.

Table 1. Chemical compositions of materials used

Specimen	C	Si	Mn	P	S
A-2	0.28	0.001	0.004	0.001	0.002
A-4	0.42	0.001	0.01	0.001	0.003
A-9	0.99	0.001	0.03	0.001	0.003
S 20 C	0.25	0.26	0.60	0.021	0.011
S 50 C	0.49	0.21	0.49	0.010	0.016
S K 3	1.11	0.23	0.50	0.022	0.009

### 2. Experimental Procedures

The experiments were carried out with a "girdle" type high pressure apparatus which had been described in detail in previous papers.<sup>12,13</sup> Two specimens, 3 mm in diameter and 3 mm in length, were inserted into a graphite tubular resistance furnace of nearly the same size with them, and were surrounded by pressure transmitting media such as talc and pyrophyllite to compose the pressure cell.

The pressure in the cell was calibrated at room temperature by measuring the press load required to induce the transitions of Bi (I-II) at 25.4 kbar, Tl (II-III) at 37 kbar, and Ba(II-III) at 59 kbar.

The temperature in the cell was measured with an alumel-chromel thermocouple, because the thermal electromotive force of this couple is less affected by pressure than that of others,<sup>14</sup> and the correction was done by the Hanneman's method.<sup>14</sup>

The isothermal transformation under high pressure was carried out according to the following program; the specimens were pressurized up to a proposed pressure at room temperature, austenitized at 950°C for 20 min, rapidly cooled to 650° or 250°C, held for various time up to 24 hr, quenched to the room temperature and finally released the pressure.

By switching off the electric current for heating directly the graphite furnace, the cooling rate of the specimen from 950° to 200°C was attained to about 200°C/sec.

The microstructure was examined by optical and electron microscopy, and TTT diagrams at 29 and 38.5 kbar were determined. The change of the characteristic points in Fe-C alloys and steels was calculated beforehand; on the former,  $A_1$  points by Kaufman's method<sup>10</sup> and  $M_s$  points by Radcliffe's equation<sup>11</sup> as shown in Fig. 1, while on the latter,  $M_s$  points by Predmore's equation.<sup>15</sup>

In order to observe the microstructure transformed under high pressure by transmission electron microscopy, discs of 0.3 mm thick were cut out from the treated specimens and thin foils were prepared by chemical and electrolytic polishing.

## III. Results

### 1. Fe-0.28%C(A-2) Alloy and S20C Steel

The A-2 alloy and S20C steel were expected to show the entirely eutectoid structure at the examined

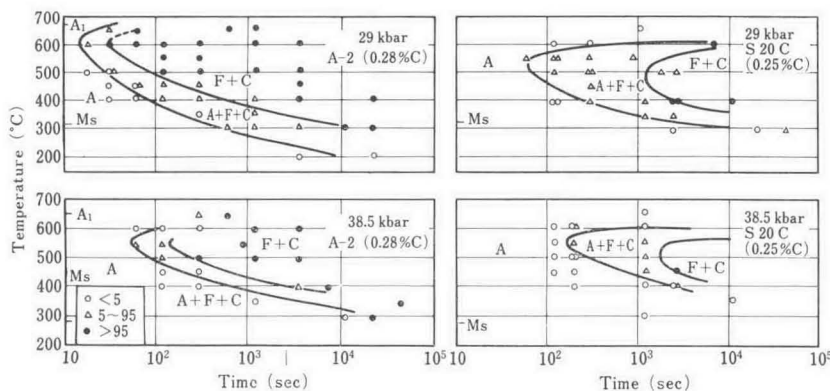


Fig. 2. TTT diagrams obtained in Fe-0.28%C alloy and 0.25%C commercial steel under high pressure

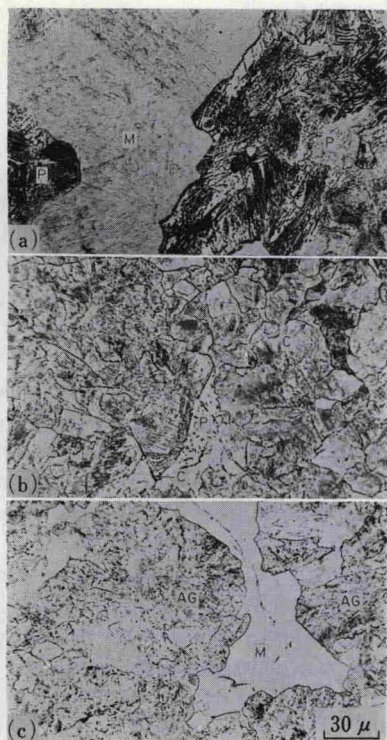


Photo. 1. Microstructures observed in Fe-0.28%C alloy treated isothermally at 29 kbar

- (a) Pearlite (P) in martensite matrix (M); 650°C × 30 sec
- (b) Pearlite (P) and carbide (C); 600°C × 2 min
- (c) Aggregate structure (AG) in martensite matrix (M); 500°C × 2 min

high pressure. The TTT diagrams obtained at 29 and 38.5 kbar are shown in Fig. 2. These diagrams show nearly the same C-shaped curve with that of a eutectoid steel at 1 atm. It is shown in these diagrams that, by an increase of the pressure from 29 to 38.5 kbar, the incubation time generally increased about five times and the temperature at the nose lowered to about 25°C.

This temperature drop at the nose was nearly equal to the drop of  $A_1$  temperature caused by above increase of pressure. Comparing the incubation time before the transformation starts in A-2 alloy with that in S20C steel at the same pressure level, the latter shows far larger retardation on the progress of transformation. Such a difference is thought to be due to the effect of impurities in S20C steel, because the grain size in both specimens was identical. In this experiment, as the measurement of austenite grain size under high pressure was very difficult, it was estimated from the martensite structure obtained by quenching the specimens from austenitized temperature.

The microstructures observed in A-2 alloy isothermally transformed at 29 kbar are illustrated in Photo. 1. Photograph 1 (a) and (b) show the example of structures transformed in a temperature range above the nose, in which range wholly pearlitic structure would be expected.

In Photo. 1 (a), it is observed that the alloy did not fully transformed yet and the structure is a mixture of pearlite and martensite. In this photograph, no

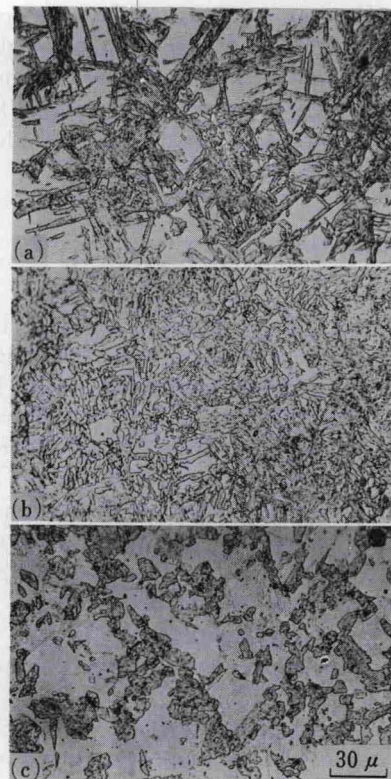


Photo. 2. Microstructures observed in Fe-0.28%C alloy (a) and 0.25%C steel (b), (c) treated isothermally under high pressure

- (a) Columnar bainite; 29 kbar, 300°C × 10 min
- (b) Columnar bainite; 29 kbar, 350°C × 20 min
- (c) Aggregate; 38.5 kbar, 450°C × 20 min

proeutectoid ferrite or carbide are observed. On the other hand, Photo. 1 (b) shows the structure after completely transformed, and the arrows indicate the carbides precipitated at prior austenite grain boundaries or sub-boundaries. These precipitates increased with an increase of the holding time. However, this tendency was weakened when the pressure was increased or the commercial steel was subjected to the experiment.

Photograph 1 (c) shows a singular structure obtained at the temperature below the nose. This structure consists of a gathering of irregular-shaped ferrite and carbide, and is similar to the one which was already reported by Radcliffe<sup>5)</sup> as "aggregate" structure. Photograph 2 shows the other singular structures which were obtained after the isothermal transformation in a temperature range a little higher than  $M_s$ . This range corresponds to the one in which the acicular bainite would be expected at atmospheric pressure. Nilan<sup>6)</sup> named this structure as "columnar bainite". In these photographs, typical columnar bainite structure is observed in both Photos. 2 (a) and (b). However, the columnarity of this structure decreased with an increase of pressure as shown in Photo. 2 (c), and the structure became rather resembled to the "aggregate".

## 2. Fe-0.42%C(A-4) Alloy and S50C Steel

These materials were chosen on the basis of an expectation that the structure would be changed from

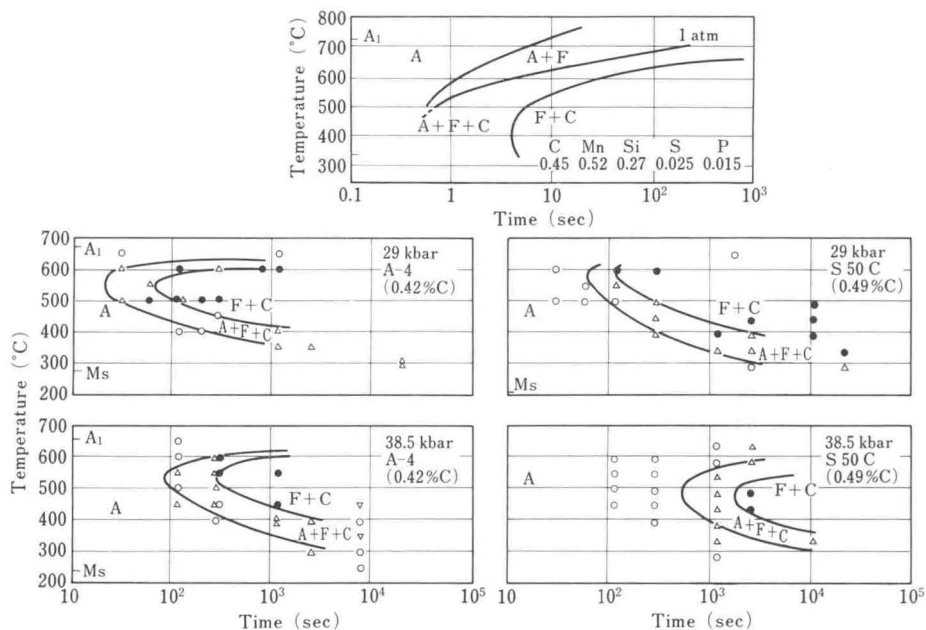


Fig. 3. TTT diagrams obtained in Fe-0.42% C alloy and 0.49% C commercial steel under high pressure. For comparison, a diagram<sup>16)</sup> of 0.45% C steel at 1 atm is quoted at the top

hypo- to hypereutectoid accompanied with the increase of pressure from 1 atm to 29 or 38.5 kbar. The TTT diagrams obtained at 29 and 38.5 kbar on these materials are shown in Fig. 3, and at the same time, a diagram on a 0.45% C steel at 1 atm is also quoted<sup>16)</sup> in this figure for reference. The diagrams under high pressure show only C-shaped curves similar to those in Fig. 2, and do not show any starting curve for the primary precipitation of carbide. The reason why these results were obtained can be explained as follows; although the carbon content in these specimens was chosen on the basis described above, as the quantity and size of the proeutectoid carbides precipitated under high pressure were too small and too fine, so that it was difficult to determine the position of the beginning of precipitation on the curve correctly.

When the incubation time at 500°C in the S50C steel transformed isothermally at high pressures is compared with that at 1 atm, it is noted that the former is about 200 times at 29 kbar and 1 000 times at 38.5 kbar longer than the latter. These values are larger than the one reported by Nilan<sup>6)</sup> on a 0.44% C steel at 24 kbar. This fact is thought to be due to the differences in the examined pressure and the composition of specimen, especially in its impurities. Actually, the diagram of the high purity A-4 alloy at 38.5 kbar is in considerably good agreement with that of the Fe-0.41% C alloy at 42 kbar in Radcliffe's paper.<sup>5)</sup> Consequently, if the differences in these conditions and additionally the procedure for applying high pressure are taken into consideration, the results obtained in this study can be asserted to be not so widely different from those which were reported hitherto.

The microstructures of the S50C steel transformed isothermally at a temperature higher than the nose are shown in Photo. 3. In these photographs, Photo. 3 (a) shows the proeutectoid ferrite formed at 700°C for 2 min at 1 atm. On the other hand, Photos. 3 (b) and (c) show the proeutectoid carbide precipitated at

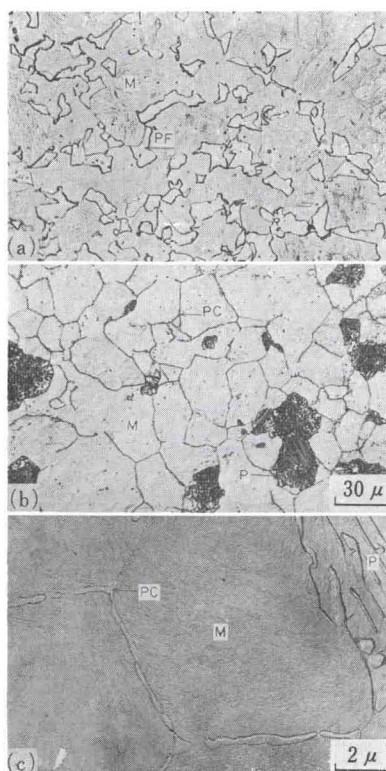


Photo. 3. Comparison of the transformation products formed in 0.49% C steel at 1 atm and 38.5 kbar  
(a) Proeutectoid ferrite (PF) in martensite matrix (M); 1 atm, 700°C × 2 min  
(b), (c) Proeutectoid carbide (PC) and pearlite (P) in martensite matrix (M); 38.5 kbar, 650°C × 1 hr

austenite grain boundary and the pearlite in a treatment at 650°C and 38.5 kbar for 1 hr, and it was confirmed that such hypereutectoid structure would be expected by pressurizing the specimen without increasing the carbon content, although it showed a hypoeutectoid structure originally at 1 atm.

Photograph 4 shows the structures obtained in a temperature range below the nose. In Photo. 4 (a),

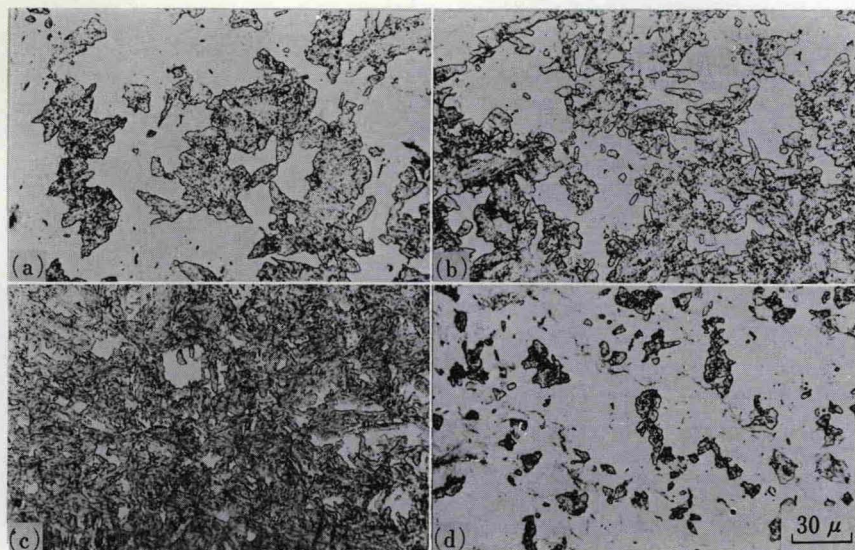


Photo. 4. Microstructures observed in Fe-0.42%C alloy (a), (b), (c) and 0.49%C steel (d) treated isothermally under high pressure (a) Aggregate; 29 kbar, 400°C x 20 min (b) Columnar bainite; 29 kbar, 350°C x 20 min (c) Aggregate; 38.5 kbar, 350°C x 3 hr (d) Aggregate; 29 kbar, 350°C x 1 hr

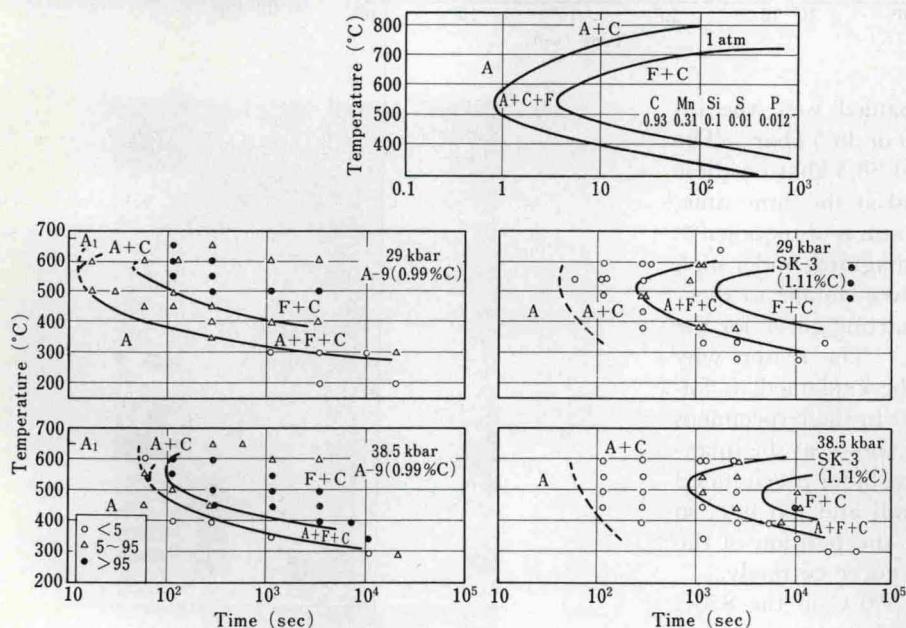


Fig. 4. TTT diagrams obtained in Fe-0.99%C alloy and 1.11%C commercial steel under high pressure. For comparison, a diagram<sup>17)</sup> of 0.93%C steel at 1 atm is quoted at the top

the "aggregate" structure which was obtained in the A-4 alloy at 400°C and 29 kbar, and is almost similar to that in Photo. 1 (b), is shown. With a decrease of temperature, the morphology of structure in the alloy became more columnar, and Photo. 4 (b) shows the "columnar bainite" observed at 350°C and 29 kbar. However, the columnarity of bainite decreased when the pressure was increased to 38.5 kbar and the temperature was kept at 350°C, as shown in Photo. 4 (c). On the other hand, when the S50C steel was examined at 350°C and 29 kbar, the observed structure was rather similar to aggregate than columnar as shown in Photo. 4 (d). Consequently, it was understood that the columnarity of bainitic structure depended on the temperature and the pressure at which the specimen had transformed, and also on the quantity of impurities in the materials.

### 3. Fe-0.99%C(A-9) Alloy and SK3 Steel

As these materials contain the corresponding carbon to obtain the hypereutectoid structure both at

1 atm and at high pressure, it is expected that the volume fraction of proeutectoid carbide must be larger at high pressure than at 1 atm. The TTT diagrams on these materials at high pressures are shown in Fig. 4, and a diagram on a 0.93%C steel at 1 atm is also shown in this figure for reference.<sup>17)</sup>

These diagrams at high pressures have an essentially similar tendency to those shown in III. 1 and III. 2, that is to say, when a diagram at 1 atm is compared with the others in Fig. 4, differences are recognized not only in the incubation time but also in the temperature range in which the carbide was formed. It is already known that the decomposition of austenite to carbide and ferrite accompanies with a decrease of volume. According to Kaufman,<sup>10)</sup> the volume decrease of 0.42 cm<sup>3</sup> took place at 996°K as the result of the precipitation of 0.25 mol of Fe<sub>3</sub>C from 0.75 mol of austenite in which 0.25 mol of carbon had been contained. This fact suggests that the Fe<sub>3</sub>C which is having higher density than other phases is easier to be formed at high pressure. Actually, as can be seen

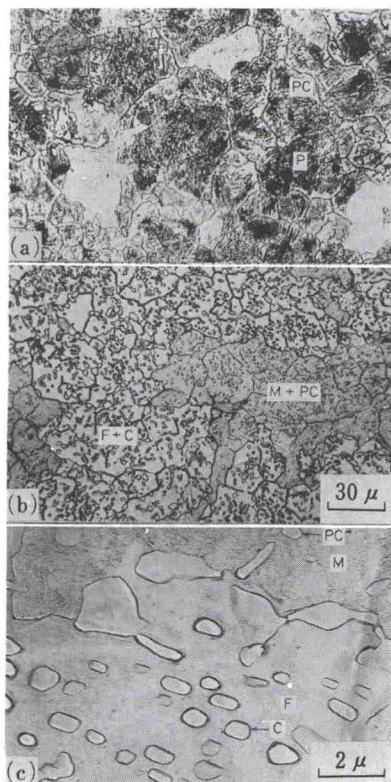


Photo. 5.

Microstructures observed in Fe-0.99%C alloy treated isothermally under high pressure

- (a) Proeutectoid carbide (PC) and pearlite (P); 29 kbar, 650°C × 2 min  
 (b), (c) Proeutectoid carbide in martensite matrix (M+PC) and coarse proeutectoid carbide in ferrite matrix (F+C); 38.5 kbar, 650°C × 1 hr

in Fig. 4, the area A+C spreads wider with an increase of pressure.

Photographs 5, 6, 7, and 8 show the microstructure of the materials transformed isothermally at high pressures. Photograph 5 shows the microstructures of A-9 alloy appeared in a temperature range higher than the nose. Photograph 5 (a) shows a microstructure obtained at 650°C and 29 kbar, and it is similar to a generally observable structure in a hypereutectoid steel at 1 atm. When the pressure was increased to 38.5 kbar, the alloy showed a entirely different structure as shown in Photos. 5 (b) and (c). Namely, although the specimen was thought to be in the midst of the transformation in this case, the observed structure was consisted of ferrite (white) and martensite (dark) with fine carbide particles precipitated on the whole surface, instead of the eutectoid products such as pearlite. Of course, the martensite in this structure was the one which had been transformed from the untransformed austenite after the isothermal treatment. This result suggests that these ferrite and carbide were separately transformed or precipitated from austenite and then grown, and did not pass through the eutectoid reaction. As the quantity of

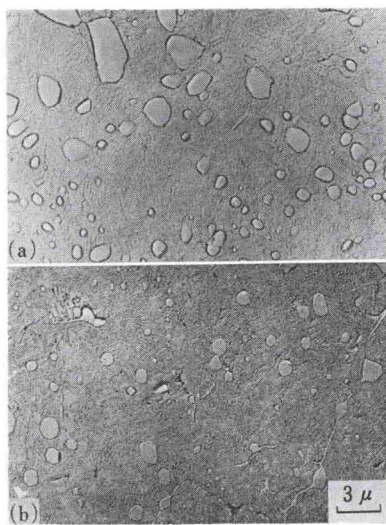


Photo. 6.

Spherical carbide in martensite matrix observed in Fe-0.99%C alloy (a) and 1.11%C steel (b) treated isothermally under high pressure

- (a) 38.5 kbar, 450°C × 2 min  
 (b) 29 kbar, 550°C × 2 min

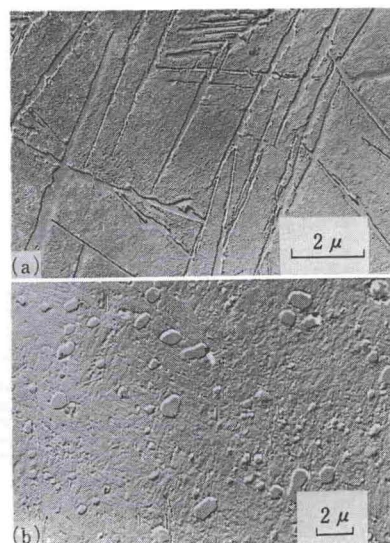


Photo. 7.

Electron micrographs of carbide in 1.11%C steel treated isothermally for 20 min at 500°C and 38.5 kbar after austenitized at 1050°C (a) and 950°C (b)

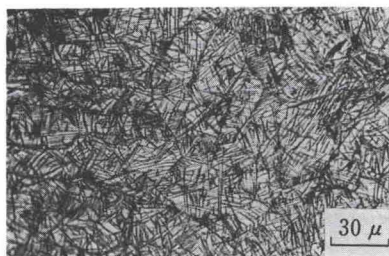


Photo. 8. Acicular carbide observed in 1.11%C steel treated isothermally for 30 min at 500°C and 38.5 kbar

the precipitated proeutectoid carbide would increase with an increase of pressure, so that the carbon content in austenite after the precipitation must be become lower. Thus the "diluted" carbon in austenite would be precipitated at the proeutectoid carbide existed already before or in the midst of the  $\gamma \rightarrow \alpha$  reaction.

Although the structure similar to the one in Photos. 5 (b) or (c) is scarcely observed on the specimen heat treated at atmospheric pressure except in the case of spheroidizing annealing, it is not difficult to obtain such a structure in high pressure treatment. The reason for this is thought to be that the driving force for promoting pearlitic transformation at this temperature would be relatively decreased with the drop of  $A_1$  temperature caused by an increase of pressure.

On the other hand, the shape of the carbide particles observed in SK3 steel changed from spherical to acicular depending on the applied pressure and temperature. Namely, the carbide precipitated at 29 kbar was always identical in its shape to the one obtained in the A-9 alloy regardless of its austenitized or transformed temperature as shown in Photo. 6, but when

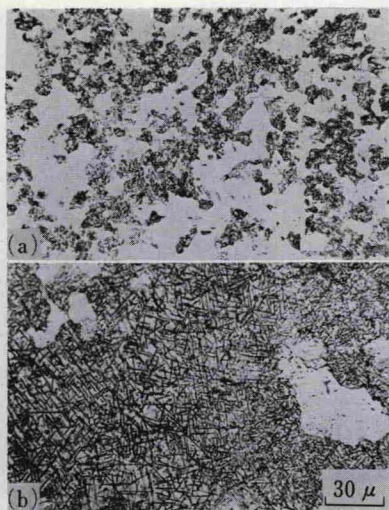


Photo. 9. Microstructures observed in Fe-0.99%C alloy (a) and 1.11%C steel (b) treated isothermally at 38.5 kbar

- (a) Carbide and aggregate; 500°C×2 min
- (b) Carbide and aggregate; 450°C×3 hr

the pressure was increased to 38.5 kbar, either spherical or acicular carbide was observed in the specimen austenitized at 950°C and then transformed at 500°C. The electron micrographs in Photo. 7 show that this change of the shape of carbide was affected by the austenitizing temperature prior to the isothermal transformation under high pressure. It seems that when the austenitizing temperature was relatively lower, the pre-existed carbides remained indissolve and the spherical carbides were grown from them during the isothermal treatment, and oppositely that when the pre-existed carbides dissolved completely in the austenite matrix at relatively higher temperature, the newly nucleated acicular carbides would be formed. It is also implied that under the pressure of about 40 kbar the A<sub>cm</sub> line would exist at 950°C for this steel, and this could result in the formation of these two shapes of carbide according as a slight difference of the experimental conditions. However, as described above, such a change was observed only in the commercial steel SK3 and did not in the high purity alloy A-9. Although it will be discussed later again, the true reason for this phenomenon is not obvious yet. Only for the SK3 steel at 38.5 kbar, the austenitizing temperature was increased to 1 050°C in this study. Photograph 8 shows a typical acicular carbide structure obtained in SK3 steel.

The structures of the A-9 alloy and SK3 steel transformed isothermally at a temperature below the nose and at 38.5 kbar are shown in Photo. 9. These are the "aggregate" structures containing the primarily precipitated carbides, and no "columnar bainite" could be observed in these high carbon specimens even though the pressure was decreased to 29 kbar.

#### 4. Summary of the Structures

The structures obtained at examined high pressures are summarized in Tables 2 and 3. In these tables

Table 2. The temperature range in which various structures are observed in isothermal transformation of Fe-C alloys under high pressures. Experiments were carried out at every 50°C. Data at 1 atm are also shown for reference.

Sample	A-2		(1)	A-4		(2)	A-9	
Pressure °C	29 kbar	38.5 kbar	1 atm	29 kbar	38.5 kbar	1 atm	29 kbar	38.5 kbar
700			↑↑			↑↑		
650	↑	↑	F P	↑	↑	↑	↑	↑
600	P	P		P	P	C	C	C
550								
500	↑	↑		↑	↑	↑	↑	↑
450	AG	AG		AG	AG	FB	AG	AG
400								
350	CB	CB		CB		AB		
300								

\* P=pearlite, AG=aggregate, CB=columnar bainite, C=carbide, F=ferrite, FB=feather bainite, AB=acicular bainite

\*\* Samples

- (1) 0.50%C, 0.001%Mn, 0.01%Si (by Scott)<sup>18)</sup>
- (2) 0.87 to 0.89%C (by Kahles)<sup>19)</sup>

Table 3. The temperature range in which various structures are observed in isothermal transformation of commercial steels under high pressures. Experiments were carried out at every 50°C. Data at 1 atm are also shown for reference.

Sample	(1)	S 20 C		(2)	S 50 C		(3)	SK 3	
Pressure °C	1 atm	29 kbar	38.5 kbar	1 atm	29 kbar	38.5 kbar	1 atm	29 kbar	38.5 kbar
700	↑↑			↑↑			↑↑		
650	F P			F P					
600		P	P		P	C P	C	C P	C F
550									
500									
450		AG	AG	FB			FB		
400					AG	AG		AG	AG
350									
300		CB	CB				AB		

\* P=pearlite, AG=aggregate, CB=columnar bainite, C=carbide, F=ferrite, FB=feather bainite, AB=acicular bainite

\*\* Samples

- (1) 0.25%C, 0.54%Mn, 0.022%P, 0.035%S, 0.14%Si (by Christenson)<sup>20)</sup>
- (2) 0.5%C, 0.91%Mn (by Wilks)<sup>21)</sup>
- (3) 1.18%C, 0.76%Mn, 0.011%P, 0.029%S, 0.029%Si, 0.009%Mo (by Blanchard)<sup>22)</sup>



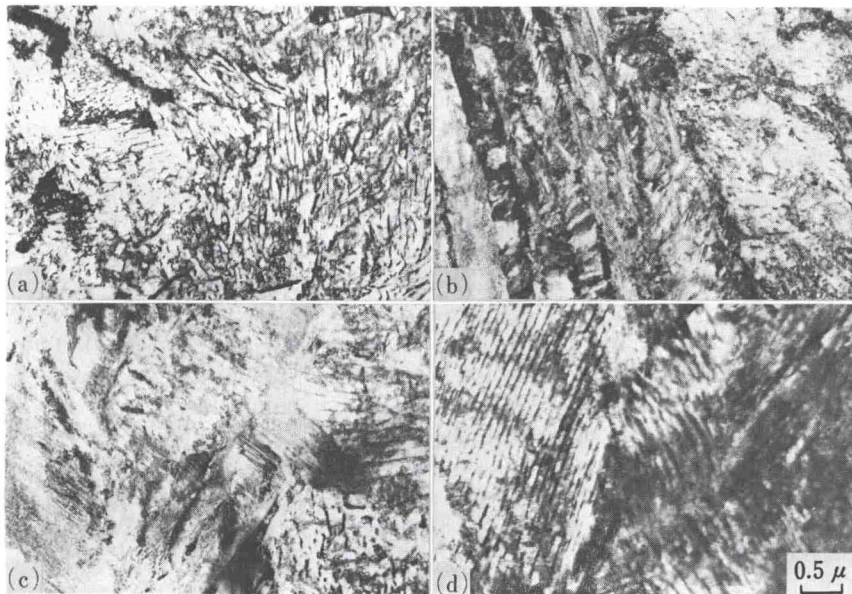


Photo. 10.

Transmission electron micrographs of structures in Fe-C alloys treated isothermally under high pressure

(a) Aggregate; Fe-0.99%C alloy, 29 kbar, 450°C × 1 min

(b) Aggregate; Fe-0.42%C alloy, 38.5 kbar, 450°C × 2 min

(c) Aggregate; Fe-0.28%C alloy, 29 kbar, 500°C × 30 sec

(d) Columnar bainite; Fe-0.28%C alloy, 29 kbar, 300°C × 3 hr

the data at atmospheric pressure are also shown for comparison.

Since the experiments were carried out at every 50°C, the temperatures of the occurrence of change structures were not exactly determined, and actually of these temperatures were not so clear because the mixed structures were often observed. The structures observed at higher temperatures above the nose were generally those which could be expected from the effects of pressure on the equilibrium phase diagram. However, in the A-9 alloy and SK3 steel containing higher carbon than others, some singular structures were observed while the pearlite structure does not appeared through the whole temperature range at both high pressures.

Photograph 10 shows the transmission electron micrographs of the "aggregate" and the "columnar bainite" structures observed in temperature ranges below the nose; Photos. 10 (a), (b), and (c) are the "aggregate" structures obtained in three kinds of Fe-C alloys and Photo. 10 (d) is the "columnar bainite" structure in the A-2 alloy. With an increase of carbon content, the appearance of carbides in these bainitic structures become increasingly lamellar, but the individual area of these structures is generally small and its morphology is rather cellular than lath-like. On the other hand, it is reported<sup>23)</sup> that the carbides in upper bainite obtained at 1 atm generally arrayed along the longitudinal axis of the lath. Therefore, it is possible to think that the "aggregate" structure is different from the upper bainite because the arrangement of carbides in the former is more complex than the latter. Furthermore, it is observed that each of the carbide lamellas in the "columnar bainite" arranged more regular and developed wider than in the "aggregate" structure.

#### IV. Discussions

##### 1. TTT Diagrams

The forms of the TTT diagrams obtained under

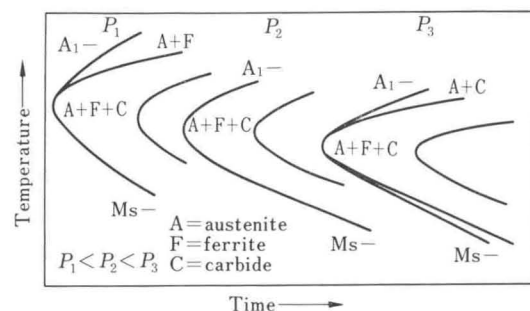


Fig. 5. Schematic illustration to the change of TTT diagram of a hypoeutectoid steel due to high pressure. Hydrostatic pressures increase from  $P_1$  to  $P_3$

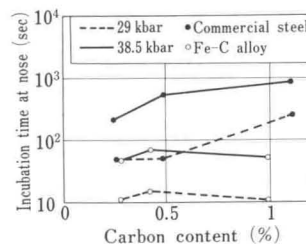


Fig. 6. Effect of pressure on the incubation time at the nose in TTT diagrams of Fe-C alloys and commercial steel

high pressure were not essentially different from that at 1 atm, and the transfer of curves with the change of carbon content or pressure could be explained on the basis of the change of phase diagram under high pressure. The temperature at the nose decreased in a same extent with a decrease of the eutectoid temperature caused by pressure. The incubation time before transformation was extended with an increase of pressure, and such retardation became more remarkable in a lower temperature range.

The representative behaviours of a TTT diagram under high pressure are illustrated schematically in Fig. 5. When the pressure increases from  $P_1$  to  $P_3$ , the characteristics of a hypoeutectoid type TTT diagram change to eutectoid or hypereutectoid type accompanying with the increasing pressure. Additionally, the incubation time increases and oppositely

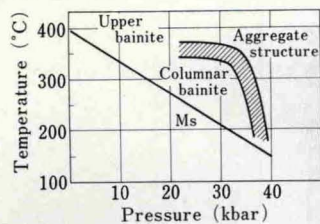


Fig. 7. Effect of pressure and temperature on the changes among various bainitic structures of Fe-0.42%C alloy

the temperature of the nose decreases at the same time. Although the decrease of the nucleation rate for the decomposition of austenite is reported<sup>5)</sup> to be far greater than that of the growth rate thereafter, when the pressure increases up to  $P_3$ , namely when the form of isothermal transformation changes to hyper-eutectoid type, it is anticipated that the decrease of the nucleation rate would be lessened by the precipitation of carbides providing nucleation sites suitable to start the transformation.

Figure 6 shows the effect of pressure on the incubation time at the nose in TTT diagrams of Fe-C alloys and commercial steels. In this figure, it is shown that the incubation time is always longer in the commercial steels than in the high purity alloys, and this tendency is entirely the same with that in the case of atmospheric pressure. With an increase of pressure from 29 to 38.5 kbar, the time before the start of transformation at the nose temperature increased by approximately five times for both materials, and there could not be detected any significant difference between these materials on the pressure dependence of the retardation. From the fact that the activation volumes for the growth of pearlite had different values between the Fe-C alloys and the commercial steels,<sup>7)</sup> it had been anticipated that the pressure dependence of the retardation on these two kinds of the materials would be different. However, as the nucleation rate would affect the start of transformation, and as the decrease of the nucleation rate is larger than that of the growth rate under high pressure, it is thought that the resultant retardation caused by an increase of pressure showed the similar tendency in both materials after set off other factors.

## 2. Microstructures

The microstructures obtained under high pressure were those which corresponded generally to the changes of the phase diagram caused by pressure. In place of the acicular bainite structure commonly observed at atmospheric pressure, some singular structures were obtained after the isothermal transformation at relatively lower temperature under high pressure. Namely, the structure changed to "columnar bainite" or "aggregate" structure with the changes of pressure and temperature. Figure 7 is the summary of the results of Radcliffe *et al.*,<sup>5)</sup> Nilan,<sup>6)</sup> and the present study, and shows the relationship between pressure and temperature on the structure changes of the A-4 alloy. The boundaries among these structures are

not clear, and are thought to be changed gradually as would be understood from Photo. 4 which showed the combined effects of pressure, temperature and composition on the change of "columnar bainite" structure. Although Nilan<sup>6)</sup> pointed out that the effect of pressure on the temperature at which "columnar bainite" would appear nearly corresponded to the one on the  $A_1$  temperature, it is not possible to explain that such structural transition was observed with an increase of carbon content as obtained in the present study. As the increase of carbon and the presence of impurities in commercial steels shifted the Ms temperature lower, and as the increase of pressure also depressed it, it is possible to think that the increase of carbon or some impurities has a similar effect to the increase of pressure. By reason of the above, the structural transition from "columnar bainite" to "aggregate" would occur with an increase of carbon content.

In regard to a temperature range which was classified in the present study as the one in which "aggregate" structure would be expected, Nilan noted in his paper that the upper bainite structure had been observed in that range. However, the transmission electron microscopy showed that the structure obtained in the present study was quite similar to the "aggregate" structure which was shown by Radcliffe *et al.* Such difference in structures may be caused by the difference in the experimental procedures.

Namely, Nilan used a tetrahedral anvil type apparatus, and on the other hand, Radcliffe *et al.* and the present authors used a piston-cylinder type and a girdle type apparatus respectively. In general, tetrahedral type is said to be suitable to obtain better hydrostatic pressure, but in the present study, no structural difference was observed between two principal directions of a specimen, parallel and perpendicular to the loading axis of the press.

When the commercial SK3 steel was treated at 29 and 38.5 kbar, the shape of the precipitated carbide changed from spherical or columnar in the case of 29 kbar to acicular in 38.5 kbar. On the contrary such change was not observed in the high purity A-9 alloy, namely, the shape of the carbide precipitated in this alloy was spherical or columnar at all these examined pressures. It is obvious from the result of Radcliffe *et al.* and of the additional experiments of the present authors that this fact cannot be attributed to the difference of carbon content in these two kinds of specimens. The exact reason is not obvious yet, but one of the cause to show the difference is possibly due to the effect of impurities contained in the SK3 steel.

As the preparation of thin foils for transmission electron microscopy was very difficult for the specimens in which the carbides were precipitated, those carbides were extracted by 5%  $\text{HNO}_3$ -ethanol solution and were determined the crystallographic structures by X-ray diffraction. As the result, both spherical and acicular carbides showed the same diffraction pattern of  $\text{Fe}_3\text{C}$ . This result would be understood from the fact that the phase  $\text{Fe}_3\text{C}$  has the largest density compared with other carbides and so that it must be

comes more stable than graphite, diamond and other type of carbides under high pressure.

### V. Conclusions

The structures obtained in the pressure range examined in the present study do not show a great difference in general compared with those which are usually obtained in the isothermal transformation at atmospheric pressure, except some changes due to the shifts in equilibrium diagram caused by pressure.

However, in a relatively lower temperature range in which acicular bainite would be expected at atmospheric pressure, the "columnar bainite" and the "aggregate" structure are observed.

It is shown that the transitional condition from "columnar bainite" to "aggregate" structure depends upon the increase of pressure or temperature and the presence of impurities in the specimen.

The rates of isothermal transformation both in the Fe-C alloys and the commercial steels are retarded by pressure over all temperature range, and the retardation is fairly larger in the latter. With increasing the pressure from 29 to 38.5 kbar in all alloys and steels, the incubation time always increases by approximately five times.

The shape of carbides in the 1.11% C commercial steel changes from spherical to acicular with an increase of pressure from 29 to 38.5 kbar, but the exact reason for this is not clear yet.

### REFERENCES

- 1) P. C. Johnson, A. B. Stein, and R. S. Davis: *J. Appl. Phys.*, **33** (1962), 557.
- 2) W. A. Bassett and T. Takahashi: ASME Paper, 64-WA/PT-24, (1964), ASME, New York.
- 3) W. Stark and G. Jura: ASME Paper, 64-WA/PT-28, (1964), ASME, New York.
- 4) F. P. Bundy: *J. Appl. Phys.*, **36** (1962) 616.
- 5) S. V. Radcliffe, M. Schatz, and S. A. Kulin: *JISI (UK)*, **201** (1963), 143.
- 6) T. G. Nilan: *Trans. Met. Soc. AIME*, **239** (1967), 898.
- 7) J. E. Hilliard and J. W. Cahn: *Progress in Very High Pressure Research*, (1961), 109, John Wiley & Sons, New York.
- 8) R. Tanaka: *Tetsu-to-Hagané*, **53** (1967), 1586.
- 9) J. E. Hilliard: *Trans. Met. Soc. AIME*, **227** (1963), 429.
- 10) L. Kaufman: *Solids under Pressure*, (1963), 303, McGraw-Hill, New York.
- 11) S. V. Radcliffe and M. Schatz: *Acta Met.*, **10** (1962), 201.
- 12) M. Suzuki and M. Fujita: *Tetsu-to-Hagané*, **53** (1967), 912.
- 13) M. Suzuki and M. Fujita: *Trans. Nat. Res. Inst. Metals*, **10** (1968), 227.
- 14) R. E. Hanneman and H. M. Strong: *J. Appl. Phys.*, **37** (1956), 612.
- 15) R. E. Predmore and E. P. Klier: *Trans. ASM*, **62** (1969), 768.
- 16) IRSID: *Courbes de Transformation*, (1956), XC42.
- 17) IRSID: *Courbes de Transformation*, (1953), XC95.
- 18) D. A. Scott, W. M. Armstrong, and F. A. Forward: *Trans. ASM*, **41** (1949), 1145.
- 19) J. F. Kahles: *Trans. ASM*, **38** (1947), 618.
- 20) A. L. Christenson, E. C. Nelson, and C. E. Jackson: *Trans. Met. Soc. AIME*, **162** (1945), 606.
- 21) C. R. Wilks: *Trans. ASM*, **35** (1945), 1.
- 22) J. R. Blanchard, R. M. Parke, and A. J. Herzig: *Trans. ASM*, **31** (1943), 849.
- 23) D. N. Shachleton and P. M. Kelly: *Iron and Steel Inst. Special Report No. 93*, (1965), 126.