On the Structure of the Steel Carburized by Various Hydrocarbons.

By Hiroshi Sawamura.

Synopsis.

Under the probable assumption that one of the chief causes for the formation of the abnormal structure in carburized steel exists in O_2 contained in steel in large quantity, the author carried out some experiments to prevent the formation of the structure in question. As the specimens, Armco iron was first adopted which was determined by analysis to have 0.067 per cent. of O_2. It was found that the abnormal structure was scarcely developed in the specimens which were carburized in some gaseous hydrocarbons such as CH_4, C_2H_4 or C_2H_2 and in CO containing the vapour of liquid hydrocarbons such as C_6H_6, C_7H_8, C_5H_{12}, C_6H_{14}, C_7H_{16} or C_8H_{18} in spite of its prevailing in those carburized by some commercial solid carburizers and in the mixture of charcoal and 40 per cent. of $BaCO_3$. These phenomena can be easily understood if the assumption before mentioned is true, because hydrocarbons deoxidize and carburize steel simultaneously at high temperatures.

The 3 kinds of other commercial steel were then carburized with C_2H_2 and CO containing C_6H_6 or C_5H_{12} which were found to be very effective for the improvement of the structure of carburized steel in the preceeding experiments. A similar effect from these carburizers, however, was not observed in this case, notwithstanding the fact that the oxygen content of these steel specimens is less than or almost equal to that of Armco iron. This is doubtless due to the fact that the cause for the formation of the abnormal structure in carburized steel is not so simple as before assumed.

Introduction.

It is a well known fact that an abnormal structure appears often in carburized steel, and when the steel having such a structure is hardened, many soft spots are liable to be produced on the carburized surface which will create various defects when it is used. The theory explaining the formation of the abnormal structure has been studied by many investigators, but it is not yet generally agreed upon. The oxygen contained in steel, however, has been proved by many researches[1] to have an intimate relation to the structure in question, although the results of experiments by some investigators[2] showed a negative proof. Especially Inoue[3], who believes that the oxygen in steel is the principal cause for the formation of the abnormal structure, found the fact that the structure of a steel containing 0.07 per cent. of carbon becomes abnormal after carburization with charcoal when the oxygen content of the material is higher than 0.07 per cent.

Grossmann[4] noted the phenomenon that the oxygen content in a steel is increased after it is carburized in the mixture of charcoal and barium carbonate.

In the present investigation, the experiments on carburization of steel were carried out with various hydrocarbons which may carburize and deoxidize steel simultaneously, in order especially to confirm their effect on the structure after carburization, under the probable assumption that one of the principal causes for the formation of the abnormal structure is the oxygen contained in steel.

Materials used.

Armco iron was used as a principal material throughout the present investigation, its composition being shown in Table I.

Table I.

Kind of material	Material No.	Composition (%)					
		C	Si	Mn	P	S	O_2
25 m.m. bar (Japanese)	I	0.17	0.30	0.42	0.048	0.021	0.015
10 m.m. bar (Japanese)	II	0.05	0.20	0.40	0.050	0.023	0.070
25 m.m. bar (Swedish)	III	0.05	0.27	0.35	0.010	0.021	0.027
25 m.m. bar (Armco iron)	IV	0.016	0.03	0.04	0.003	0.011	0.067

The other materials given in Table I were also used supplementally. The oxygen content in these materials was determined by the modified Ledebur method[5] in the author's laboratory.

After the materials were turned on their surface, they were machined to the size of about 10 m.m. and one each surface of the specimens

1) Ehn, Jour. Ir. St. Inst., 1922 No. I, 157.
Gat, Trans. Am. Soc. St. Tr., **12** (1927) 376.
Inoue, Tetsu to Hagane, **15** (1928) 287; Mem. Coll. Eng. Kyushu Imp. Univ., **5** (1928) 1.
Grossmann, Trans. Am. Soc. St. Tr., **16** (1929) 1, Trans. Am. Soc. St. Tr., **18** (1930) 601.
2) Epstein and Rawdon, Trans. Am. Soc. St. Tr., **12** (1927) 337.
3) Loc. cit.
4) Loc. cit.
5) Mem. Coll. Eng. Kyoto Imp. Univ., **9** (1936) 117.

thus made was polished by a No. 02 polishing paper as the carburizing test surface.

Carburizing experiments on the materials with some commercial carburizers.

The materials given in Table I were carburized by some commercial carburizing materials and the resulting carburized structure was studied in order to make the results of the following experiments clearer.

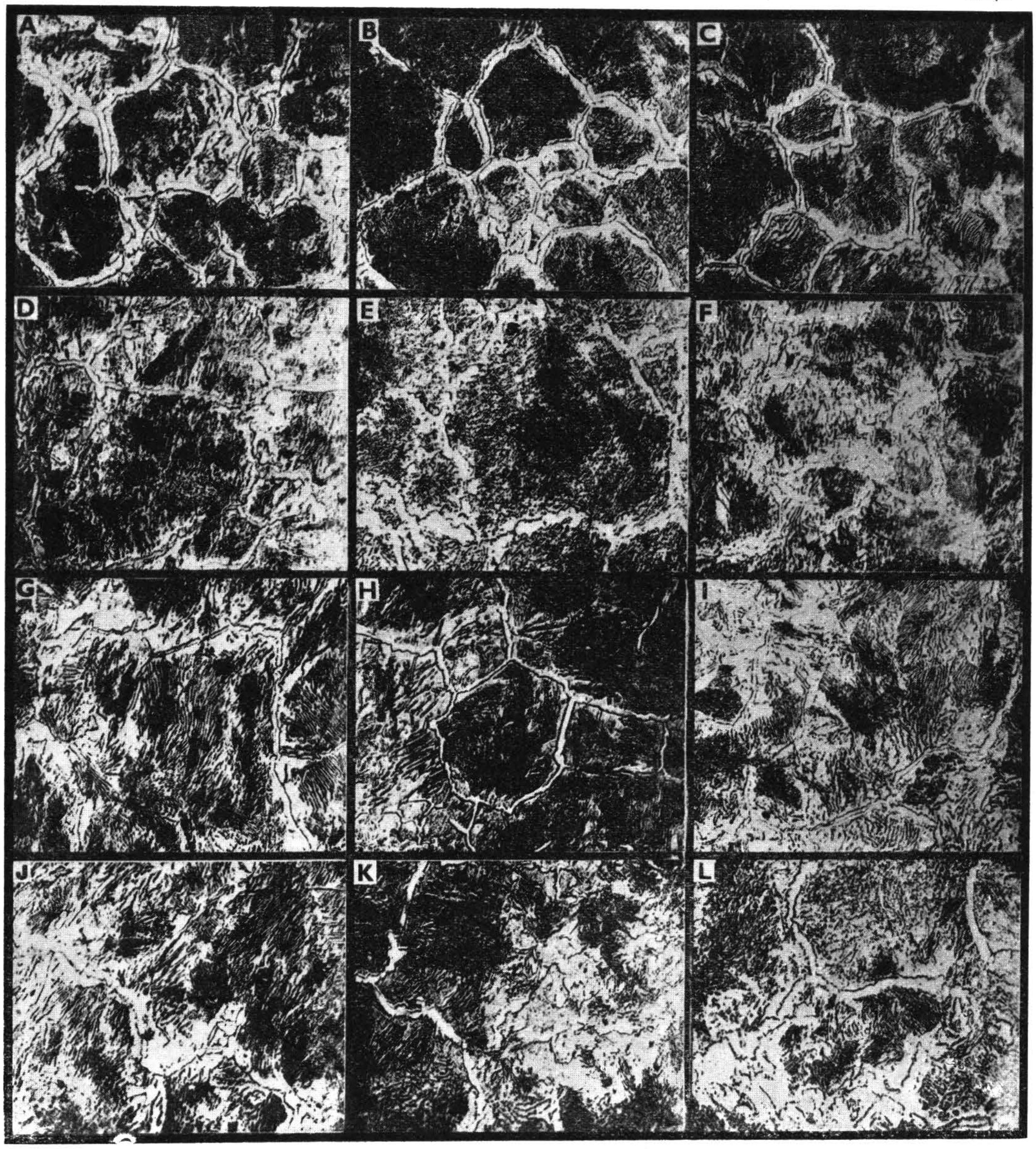
Experimental method.—The corburizing materials adopted for this purpose were as follows:

Hardenite.........The mixture of pine charcoal powder of 8 to 20 meshes and 40 per cent. by weight of barium carbonate.

G T carburizer...Made by "Nippon Netsuren Kogyosho" (Japanese Factory for Materials for Heat Treatment).

S T carburizer....Made by S T "Netsushorizai Kenkyusho" (Research Laboratory for Materials for Heat Treatment in Japan).

Photo. 1. ×140



A (Material I GT-carburizer) B (Material I ST-carburizer) C (Material I Quick-Light)
D (Material II GT-carburizer) E (Material II ST-carburizer) F (Material II Quick-Light)
G (Material III GT-carburizer) H (Material III ST-carburizer) I (Material III Quick-Light)
J (Material IV GT-carburizer) K (Material IV ST-carburizer) L (Material IV Quick-Light)

Quick-Light "A"...Made by E. F. Houghton and Co. in U.S.A.

The specimens were packed in the middle of a cast iron carburizing pot, about 60 m.m. in dia., and about 160 m.m. long, and heated in an electric resistance furnace. The hot junction of the Pt-Pt. Rd thermocouple was placed adjacent to the specimens in the pot in which a porcelain protecting tube of the thermocouple was inserted.

Results of experiments.—The microstructure of the hypereutectoid zone of 4 kinds of the carburized specimen treated at 950°C for about 16 hours is shown in Photo. 1-A to L. We can here recognize the fact that the abnormal structure develops in all kinds of material adopted in this experiment, and also that material I has a somewhat good structure and the structure of the remainder is unusually abnormal irrespective of the carburizing material used.

Another specimen of Armco iron was heated at the rate of 15°C per minute up to 900°C and this temperature was kept constant for different intervals of time. The average thickness of the carburized zones of this specimen determined by microscopical examination is shown in Table II and their typical structures in Photo. 2-A.

Table II.

Carburizing time (Hour)	Thickness of carburized zones (m.m.)			
	Hyper-eutectoid	Eutectoid	Hypo-eutectoid	Total
2	0.05	0.25	0.65	0.95
6	0.30	0.40	0.70	1.40
10	0.55	0.50	0.95	2.00

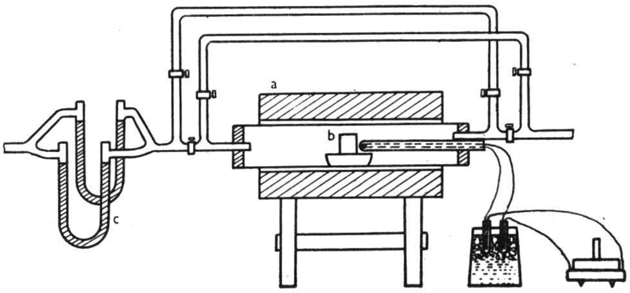
Carburizer: Hardenite, Carburizing temperature: 900°C.

Carburizing experiments on Armco iron with gaseous hydrocarbons.

Carburizing materials.—Methane (CH_4), ethylene (C_2H_4) and acetylene (C_2H_2) were adopted, among which methane and ethylene were chemically produced, i. e. the former by the reaction among sodium hydroxide, calcium oxide and sodium acetate and the latter from alcohol and orthophosphoric acid, and acetylene was a commercial product in a bomb. They were introduced in the carburizing tube after being very carefully purified and dried by the usual method.

Experimental method.—After the entire free space occupied in the apparatus was replaced by the gas in question, the latter was introduced into the porcelain carburizing tube, 35 m.m. in inner diameter, in which the sample was set in a porcelain boat at the middle of the tube. The rate of gas flow was always 2 to 2.5 liter per hour, and its direction in the carburizing tube was reversed every 30 minutes by the arrangement as shown in Fig. 1. The specimens were heated at the rate of 10°C per minute up to 900°C, and after this temperature was kept constant for a desired interval of time, they were furnace cooled.

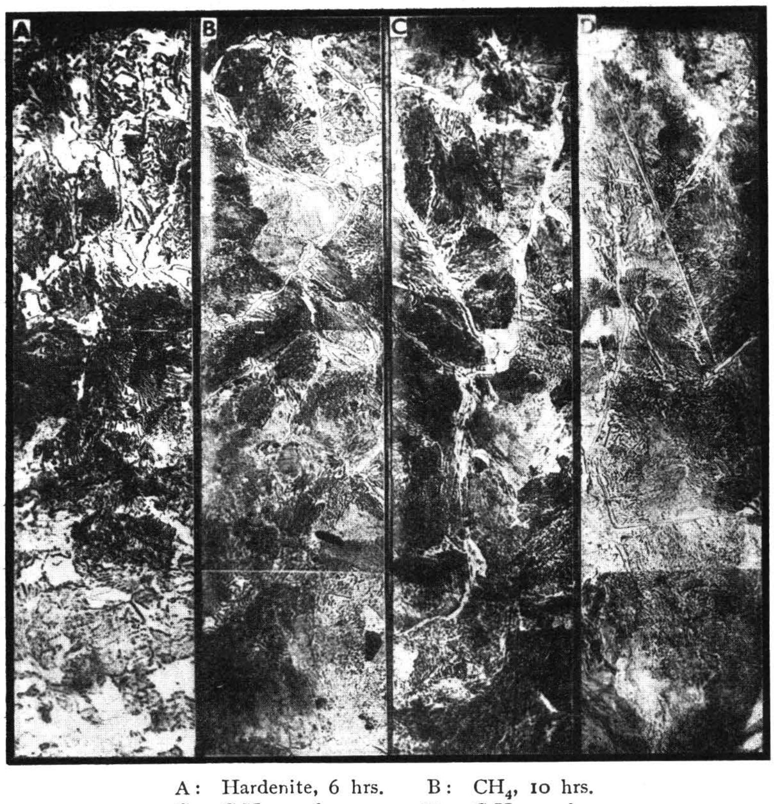
Fig. 1.



a: Electric resistance furnace, b: Specimen, c: P_2O_5

Results of experiments.—The average thickness of the carburized zones of the treated specimens is given in Table III. Their typical structure is

Photo. 2. ×125



A: Hardenite, 6 hrs. B: CH_4, 10 hrs.
C: C_2H_4, 10 hrs. D: C_2H_2, 10 hrs.

Table III.

Kind of carburizer	Carburizing time (Hour)	Rate of gas flow (Liter per hour)	Thickness of carburized zones (m.m.)				Structure
			Hopereutectoid	Eutectoid	Hypoeutectoid	Total	
CH_4	2	2	0.10	0.40	0.70	1.20	Almost normal
	6		0.40	0.50	1.00	1.90	
	8		0.40	0.60	1.30	2.30	
	10		0.50	0.60	1.60	2.70	
C_2H_4	2	2.5	0	0.13	0.29	0.42	Ditto.
	6		0	0.29	0.71	1.00	
	10		0.50	0.54	1.08	2.12	
C_2H_2	2	2.5	0	0.30	0.70	1.00	Ditto.
	6		0.35	0.30	0.80	1.45	
	10		0.70	0.60	1.40	2.70	

Carburizing temperature: 900°C.

shown in Photo. 2-B to D. As seen in these photographs, the specimens are remarkably improved in their structure when carburized by gaseous hydrocarbons.

Carburizing experiments on Armco iron with liquid hydrocarbons.

Carburizing materials.—The liquid hydrocarbons adopted in this experiment were as follows:

Benzene series.......Benzene (C_6H_6) and toluene (C_7H_8).

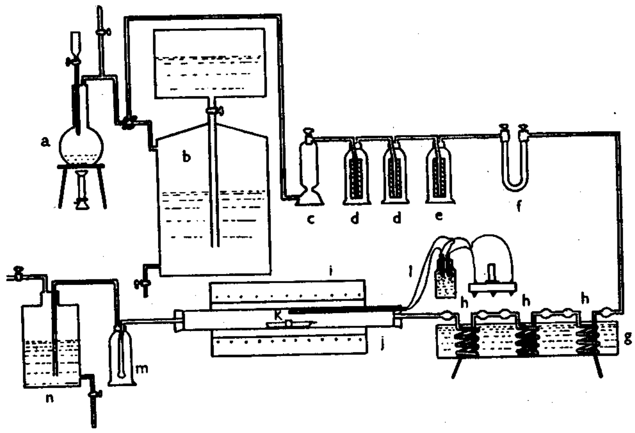
Paraffine series......Pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}) and octane (C_8H_{18}).

All reagents were the product of Merk.

Experimental method.—Liquid hydrocarbons should be first vapourized before being used for carburization. For this purpose, the author adopted the arrangement of apparatus shown in Fig. 2. In the figure, g is a water thermostat which was kept at a constant temperature of 30°C during the experiment. The liquid carburizer in question was contained in 3 Winkler's washing coils, h, connected in series in the thermostat. Some gas was passed through h at the rate of 2.4 liters per hour to be saturated with the vapour of the liquid hydrocarbon in question, and then introduced into the cardurizing tube j.

As a preliminary experiment, carbon monoxide and nitrogen respectively, saturated with the vapour of benzene, was used for carburization. Under the same conditions, the carbon content of the carburized zone was found to be far richer in the specimen carburized in carbon monoxide as was determined also by Bramly and Lawton.[1] It was also rather difficult to obtain the zone of hyper-

Fig. 2.



a: CO-generater
b: Gas reservoir
c: Soda lime
d: $Na_2S_2O_4$ solution
e: Conc. SO_4H_2
f: P_2O_5
g: Thermostat
h: Winkler's washing coil
i: Electric furnace
j: Carburizing tube (porcelain)
k: Sample
l: Pyrometer
m: Conc. SO_4H_2
n: Aspirator

eutectoid by carburizing the specimen in nitrogen. As the result of this experiment, carbon monoxide was adopted as the vehicle for introducing hydrocarbons into the carburizing tube. It was produced chemically from formic acid and concentrated sulphuric acid and carefully purified and dried in the usual manner before being introduced into the Winkler's washing coils. The carburizing temperature was 950°C. Other details of the experimental method were just the same as before.

Results of experiments.—The average thickness of the carburized zones is given in Table IV. The structure of all the carburized specimens are generally good as shown in Photo. 3-A to F. It

Table IV.

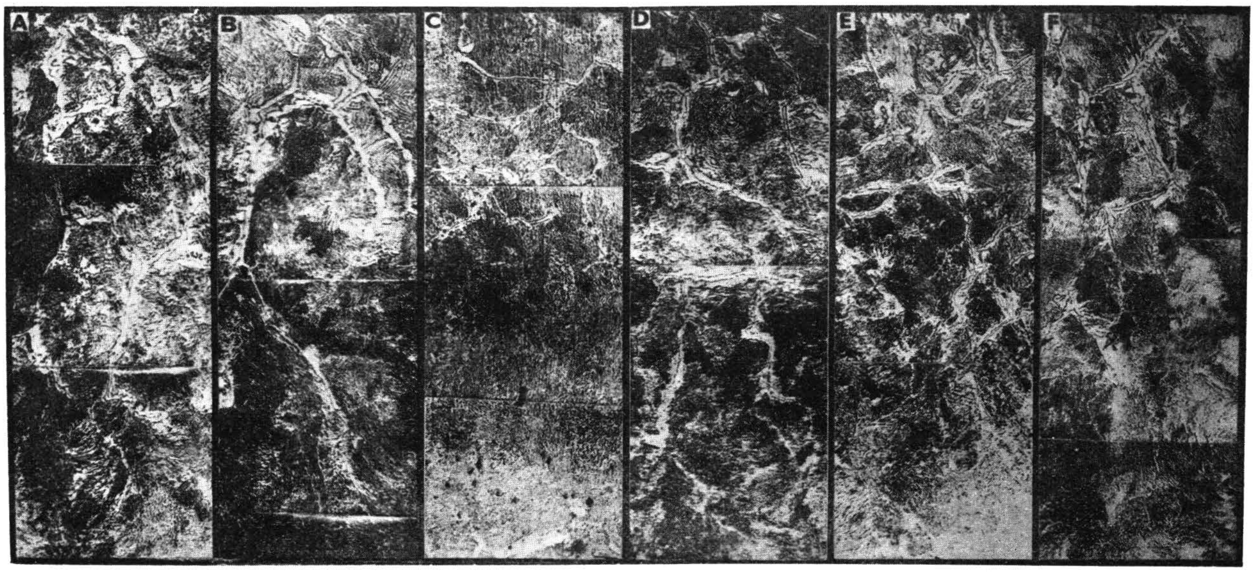
Kind of carburizer	Carburizing time (Hour)	Thickness of carburized zones (m.m.)				Structure
		Hypereutectoid	Eutectoid	Hypoeutectoid	Total	
$CO+C_6H_6$	2	0	0	0.83	0.83	—
	6	0.25	0.13	1.16	1.54	Almost normal
	10	0.58	0.54	1.46	2.58	Ditto.
$CO+C_7H_8$	2	0.21	0.25	0.67	1.13	Rather improved
	6	0.63	0.29	1.13	2.05	Ditto.
	10	0.66	0.59	1.42	2.67	Ditto.
$CO+C_5H_{12}$	6	0.48	0.29	1.13	1.90	Almost normal
$CO+C_6H_{14}$	6	0.58	0.38	1.17	2.13	Rather improved
$CO+C_7H_{16}$	6	0.56	0.27	1.29	2.12	Little improved
$CO+C_8H_{18}$	6	0.54	0.38	1.25	2.17	Rather improved

Carburizing temperature: 950°C.

1) Carnegie Scholarship Mem. (Ir. St. Inst.), (1927) 35.

Photo 3

×110



A: $CO+C_6H_6$, 10 hrs. B: $CO+C_7H_8$, 10 hrs. C: $CO+C_5H_{12}$, 6 hrs.
D: $CO+C_6H_{14}$, 6 hrs. E: $CO+C_7H_{16}$, 6 hrs. F: $CO+C_8H_{18}$, 6 hrs.

may be noted especially that the structure is almost normal in the specimens treated by benzene and pentane.

From the results of experiments hitherto carried out, the general phenomenon was confirmed that the structure of the carburized Armco iron is generally improved when it is treated by hydrocarbons, although it becomes abnormal when carburized with some commercial carburizing materials. The effect of methane, ethylene, acetylene, benzene and pentane in this direction is very remarkable.

Carburizing experiments of some carbon steels other than Armco iron by hydrocarbons.

Carburizing experiments were further carried out to find the effect of some hydrocarbons on the structure of carburized zones of 3 kinds of carbon steels other than Armco iron, their composition being given in Table I. As carburizer, acetylene, benzene and pentane were adopted. The carburizing time was always 6 hours at 950°C. Other details of the experimental method were just the same as before.

Experimental results.—The average thickness of carburized zones is given in Table V. As before mentioned, when these specimens are carburized with hardenite and some commercial carburizing materials, their structure becomes noticeably abnormal as shown in Photo 1-A to I. All the materials except Material I carburized in this experiment are also abnormal in their structure as shown in Photo. 4-A to L. In other words, the hydrocarbons used in this experiment have no effect on the structure of these steels after carburization. The structure of Material I seems to have been somewhat improved in this experiment.

Table V.

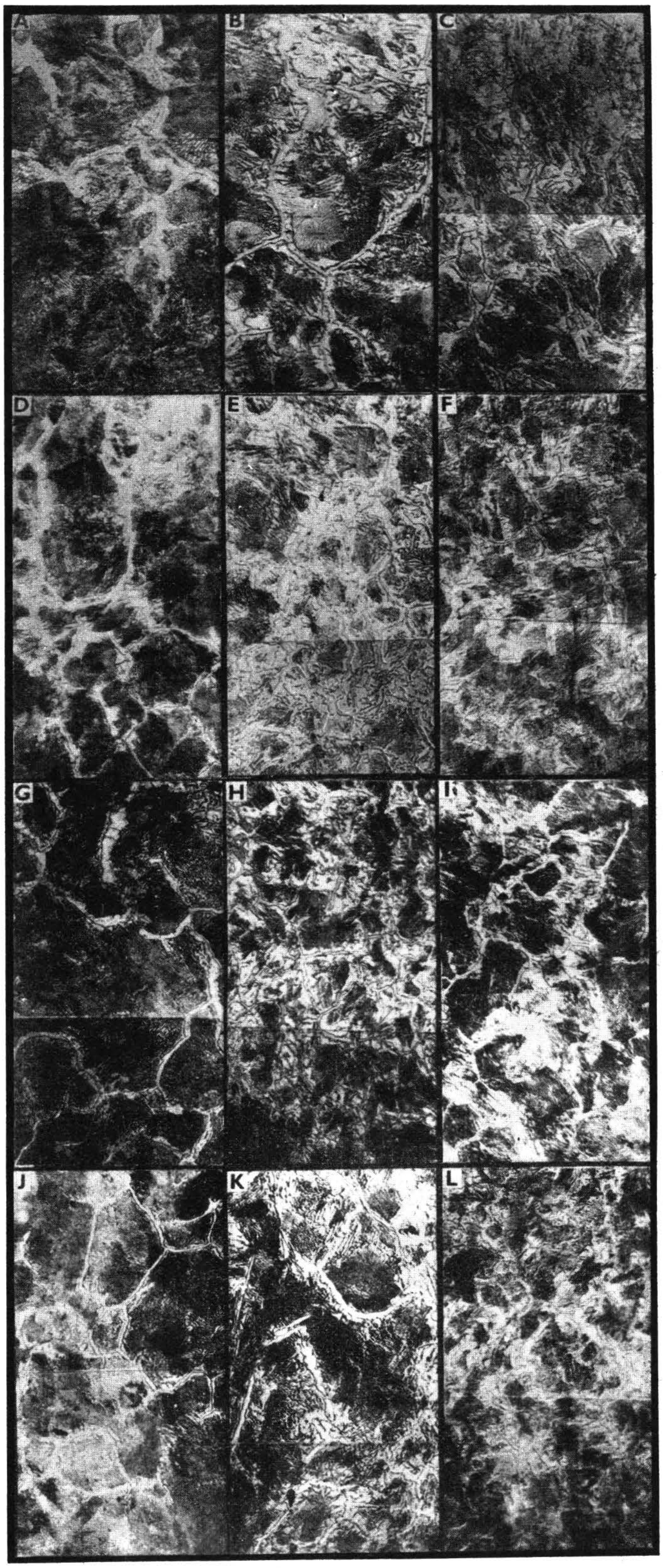
Kind of carburizer	Material No.	Thickness of carburized zones (m.m.)				Structure
		Hyper-eutectoid	Eutectoid	Hypo-eutectoid	Total	
Hardenite	I	0.50	0.29	—	—	Little improved
	II	0.46	0.25	1.21	1.92	Not improved
	III	0.46	0.29	1.33	2.08	Ditto.
C_2H_2	I	0.61	0.31	—	—	Little improved
	II	0.56	0.33	1.30	2.19	Not improved
	III	0.56	0.31	1.09	1.96	Ditto.
$CO+C_6H_6$	I	0.75	0.38	—	—	Little improved
	II	0.67	0.42	1.15	2.24	Not improved
	III	0.61	0.29	1.27	2.17	Ditto.
$CO+C_5H_{12}$	I	0.71	0.29	—	—	Little improved
	II	0.65	0.23	1.33	2.21	Not improved
	III	0.67	0.25	1.37	2.29	Ditto.

Carburizing temperature: 950°C, Carburizing time: 6 hours.

From the results of this experiment, it is evident that the effect of hydrocarbons on the structure of carburized steel has not a universal but a selective character.

As the oxygen content of Material I to III is almost equal or lower to that of Armco iron, the structure after carburization should also be normal in these materials as it is in Armco iron, after they are carburized with hydrocarbons, if the oxygen content of steel concerns only the formation of the abnormal structure. The experimental fact, however, gives a negative proof to the above consideration. Therefore, it is to be concluded that

Photo. 4. ×120



A (Material I, Hardenite) B (Material II, Hardenite) C (Material III, Hardenite)
D (Material I, C_2H_2) E (Material II, C_2H_2) F (Material III, C_2H_2)
G (Material I, $CO+C_6H_6$) H (Material II, $CO+C_6H_6$) I (Material III, $CO+C_6H_6$)
J (Material I, $CO+C_5H_{12}$) K (Material II, $CO+C_5H_{12}$) L (Material III, $CO+C_5H_{12}$)

the cause for the formation of the structure in question is not so simple as assumed during the present investigation by the author. It is due to this fact that the theory about this question is very vague at present.

Summary.

The results of the present investigation may be summarized as follows:

(1) It was confirmed that Armco iron becomes markedly abnormal in its structure when carburized with hardenite and some commercial solid carburizing materials. The structure of the same iron, however, was found to be almost normal when carburized with hydrocarbons.

(2) The above phenomenon can be understood under the probable assumption that one of the principal causes for the formation of the abnormal structure in carburized steel concerns the oxygen contained in steel.

Armco iron becomes normal in its structure after it is carburized with hydrocarbons, because carburization and deoxidation reactions may take place simultaneously in this case during the carburizing process.

(3) The above effect of hydrocarbons on the structure of carburized steel has not a universal but a selective character; it appears on some special materials such as Armco iron.

(4) From the results mentioned in (3), the cause for the formation of an abnormal structure in carburized steel is not so simple as first assumed by the author.

Acknowledgement.

The author wishes to express his sincere gratitude to the Toyoda Schokki Seisakusho, Kariya near Nagoya, under whose financial support the present investigation was carried out, and also to Mr. A. Imanishi, Mr. Y. Konaka, and Mr. K. Sawamura for their kind assistance.

(Received Nov. 10, 1935)