

Binary and ternary interstitial alloys

II. The iron-carbon-nitrogen system

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[PLATES 2 AND 3]

Chemical and X-ray investigation of the reaction of carbon monoxide with iron nitrides and of the reaction of ammonia with iron carbides discloses the existence of iron carbonitrides—a series of new ternary interstitial alloys containing iron, carbon and nitrogen. ζ -phase carbonitrides, with structures similar to those of ζ -iron nitrides, have a range of homogeneity extending approximately from Fe_3N_4 to $\text{Fe}_3\text{C}_3\text{N}$. The latter is isomorphous with Fe_2N . ϵ -phase carbonitrides, which are isomorphous with ϵ -iron nitrides, have a composition range of approximately 25 to 33 atomic % nitrogen plus carbon, i.e. from Fe_3X to Fe_2X , in which the higher carbon concentration limit is not less than 16 atomic %.

Probable phase fields for part of the iron-carbon-nitrogen system are given on a ternary diagram.

Prolonged reaction of carbon monoxide with iron nitrides results in complete elimination of nitrogen. Below 500°C the product is a carbide of iron, now called iron percarbide, the narrow composition range of which includes Fe_{20}C_9 . Above 500°C the product of the same reaction is cementite.

INTRODUCTION

Of the transition elements, columbium (Deville 1868) and titanium (Goldschmidt 1927; see Knaggs, Karlik & Elam 1932; Hume-Rothery, Raynor & Little 1942 *a, b*) give carbonitrides, but although the existence of iron carbonitrides has been suspected (Fry 1923), the only previous work on the iron-carbon-nitrogen system is an investigation of the mutual solubilities of carbon and nitrogen in α iron (Köster 1930).

Fowler (1901) passed carbon monoxide over Fe_2N at red heat and found carbon dioxide, but no cyanogen compounds, in the exit gases. He considered that iron cyanide might be formed but did not explore this possibility. The present paper describes an investigation, by chemical and X-ray methods, of Fowler's carburizing reaction and of the reverse process, that is, the nitriding of iron carbides with ammonia. Results obtained by the study of both reactions, and by heat treatment of their products, discloses the existence of iron-carbon-nitrogen interstitial alloys containing up to 25 atomic % carbon, and enables phase fields for part of the iron-carbon-nitrogen system to be given.

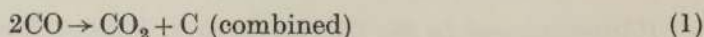
In addition, it is found that the reactions of carbon monoxide with iron nitrides provide methods for preparing cementite (Fe_3C) and pure iron percarbide (Fe_{20}C_9).

EXPERIMENTAL

Apparatus and experimental procedure

Pure carbon monoxide (Farkas & Melville 1939) was circulated for varying times by means of a glass pump (Brenschede 1936; Funnel & Hoover 1927; Livingstone 1929) over iron nitrides (prepared as described in part I and powdered to pass a

300-mesh) at various temperatures. The apparatus, shown in figure 1, consisted of a closed circulating system containing a silica reaction tube, the centre portion of which was maintained within $\pm 2^\circ \text{C}$ of the required reaction temperature and the ends of which were water-cooled. A magnetic device (see part I) enabled the silica boat containing 0.5 g. nitride to be moved between the reaction and quenching zones without opening the system. Carbon dioxide formed during the reaction



was condensed in liquid oxygen-cooled traps, and the pressure of carbon monoxide was kept at its initial atmospheric value by adding fresh gas from a burette. Thus, the volume of carbon monoxide reacted was continuously observed, and, by applying corrections for molecular nitrogen evolved, for variations in atmospheric temperature and pressure and for evaporation of liquid oxygen, the error in calculating the total volume of carbon monoxide used in any complete experiment was probably within $\pm 4\%$.

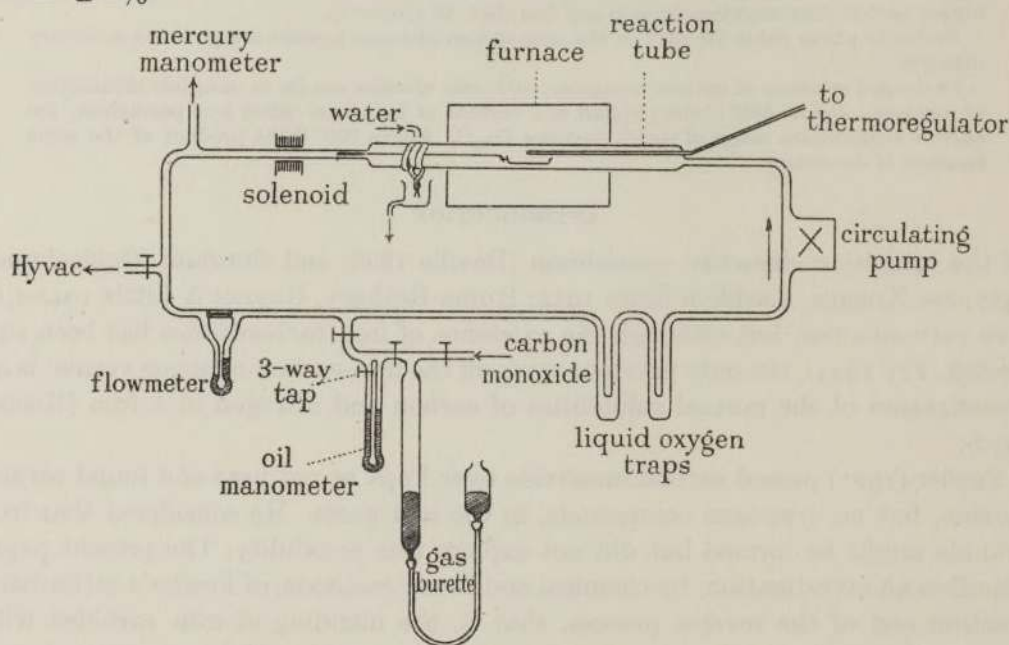
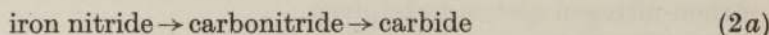
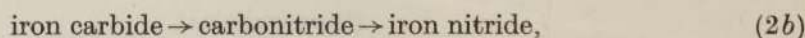


FIGURE 1. Apparatus for carburizing iron nitrides.

The experimental method therefore allowed the progress of the reaction



to be followed continuously and interrupted at any desired stage. In studying the reverse process, i.e.



iron carbides (prepared by prolonged carburizing of iron nitrides; see below) were nitrified with ammonia according to the method for preparing iron nitrides (part I).

For the heat treatment of carbonitrides and carbides a reaction tube identical with that described above was used. A 0.1 g. sample, contained in a silica boat, was

placed in the cold end of the tube. The apparatus was evacuated and the sample was then moved into the centre of the tube where it was maintained at the required temperature for a given time. Evolved nitrogen was removed at intervals by re-evacuation.

Analysis of iron carbides and carbonitrides

Except in a few cases, where there was insufficient material, nitrogen was determined by at least two of the following methods:

- (i) semi-micro-Kjeldahl method (Beet & Belcher 1938);
- (ii) micro-Dumas combustion at 800° C;
- (iii) loss in weight on heating *in vacuo* at 1000° C.

The results given have a probable error of ± 0.08 weight % N, irrespective of the amount of nitrogen present. Carbon was determined by two methods:

- (iv) micro- and, as a check in some cases, macro-combustion in oxygen at 850° C;
- (v) assuming that the total iron remained constant and that no elements other than iron, carbon and nitrogen were present, and knowing the initial and final nitrogen contents, the carbon was calculated from the difference in weight of the specimen before and after carburizing.

Since agreement between results of methods (iv) and (v) was obtained with a probable error of ± 0.2 weight % C, the assumptions made in (v) seemed valid and it was thought unnecessary to determine iron separately. In most cases, however, the ferric oxide residues from (iv) were weighed and gave results for iron in agreement with those calculated by difference. Mean values are given in tables 1 to 5 and have a probable error of ± 0.3 weight % Fe.

X-ray investigation

Powder photographs were taken at $18 \pm 2^\circ$ C with Co $K\alpha$ radiation (α_1 , 1.78529; α_2 , 1.78917 kX) in a 19 cm. Bradley-type hydrogen-filled camera. Line positions were measured and unit-cell dimensions were calculated as described in part I.

RESULTS

In the tables of results, each carburizing run is denoted by a number (C 1, C 2, etc.), which is also given to the X-ray powder photograph of the product. Experiments in which products were given subsequent heat treatment are denoted by the suffix H, so that C 6-H refers to an experiment in which the product of run C 6 was heated *in vacuo*. Experiments in which iron carbides were nitrified are similarly denoted by the suffix N. For example, photograph C 9-N, plate 3, is that of the product obtained by passing ammonia over a carbide which, in turn, was obtained in the carburizing run C 9.

The reaction of carbon monoxide with iron nitrides at 450° C (runs C 1 to C 8)

Table 1 and figure 2 show results of carburizing ϵ nitrides, containing 31 to 33 atomic % N, at 450° C for varying times from 35 min. to 47 hr. With increasing time of carburizing, the carbon concentration increases and the nitrogen concentration decreases at about equal rates. Up to a limit, at which approximately three-

TABLE 1. THE REACTION OF CARBON MONOXIDE WITH ϵ -IRON NITRIDES AT 450° C (RUNS C 1 TO C 8)

run	initial nitride		car- burizing time (hr.)	weight %			product			phases	unit-cell dimensions.			
	wt. % N	at. % N		Fe	C	N	Fe	C	N		C+N	a	b	c
C1	11.0	33.0	0.58	88.2	2.4	9.4	64.5	8.2	27.4	35.5	—	2.756	4.826	4.400
C2	10.3	31.4	1.0	88.9	2.8	8.0	66.4	9.7	23.8	33.5	—	2.752	4.824	4.403
C3	10.3	31.4	2.0	89.0	4.1	6.9	65.6	14.1	20.3	34.4	—	2.752	4.834	4.389
C4	10.3	31.4	8.0	88.8	7.0	4.4	63.9	23.4	12.6	36.0	—	2.749	4.845	4.376
C5	10.6	32.1	9.0	89.3	7.0	3.7	65.4	23.8	10.8	34.6	—	2.745	4.841	4.374
C6	10.9	32.8	25.8	88.5	10.2	1.3	62.7	33.6	3.7	37.3	—	—	—	—
C7	10.0	30.7	40.0	89.8	9.5	0.8	65.5	32.2	2.3	34.5	—	—	—	—
C8	11.0	33.0	47.3	90.9	8.5	0.7	68.2	29.7	2.1	31.8	—	—	—	—

TABLE 2. THE REACTION OF CARBON MONOXIDE WITH γ' , ϵ - AND ζ -IRON NITRIDES AT 450-700° C (RUNS C 9 TO C 14)

run	initial nitride		car- burizing time (hr.)	car- burizing temp. (°C)	weight %			product			phases		
	wt. % N	at. % N			Fe	C	N	Fe	C	N		C+N	
C9	6.5	21.7	17	450	91.0	7.5	1.5	69.0	26.5	4.5	31.0	—	χ, ϵ
C10	5.7	19.4	19	450	91.0	7.4	1.1	70.1	26.5	3.4	29.9	—	$\chi, (\epsilon)$
C11	6.2	20.9	18	470	90.7	9.3	0	67.7	32.3	0	32.3	—	χ
C12	8.2	26.3	15	500	91.2	8.8	0	69.0	31.0	0	31.0	—	χ
C13	11.0	33.0	0.5	600	92.2	7.8	0	71.8	28.2	0	28.2	—	cementite, χ
C14	11.3	33.7	0.2	700	—	15.2	0	—	—	—	—	—	carbon

quarters of the original nitrogen is replaced by carbon, the product is a single homogeneous phase, the structure of which differs only slightly from the initial ϵ -iron nitride structure. Photographs C1 to C5, plate 2, show this single phase, which gives reflexions due to a base-centred orthorhombic lattice of iron atoms, that is, a distorted hexagonal close-packing which is similar to the ζ -nitride iron atom arrangement (part I). It is therefore proposed here that the new ternary interstitial alloys of this phase should be named ζ -iron carbonitrides.

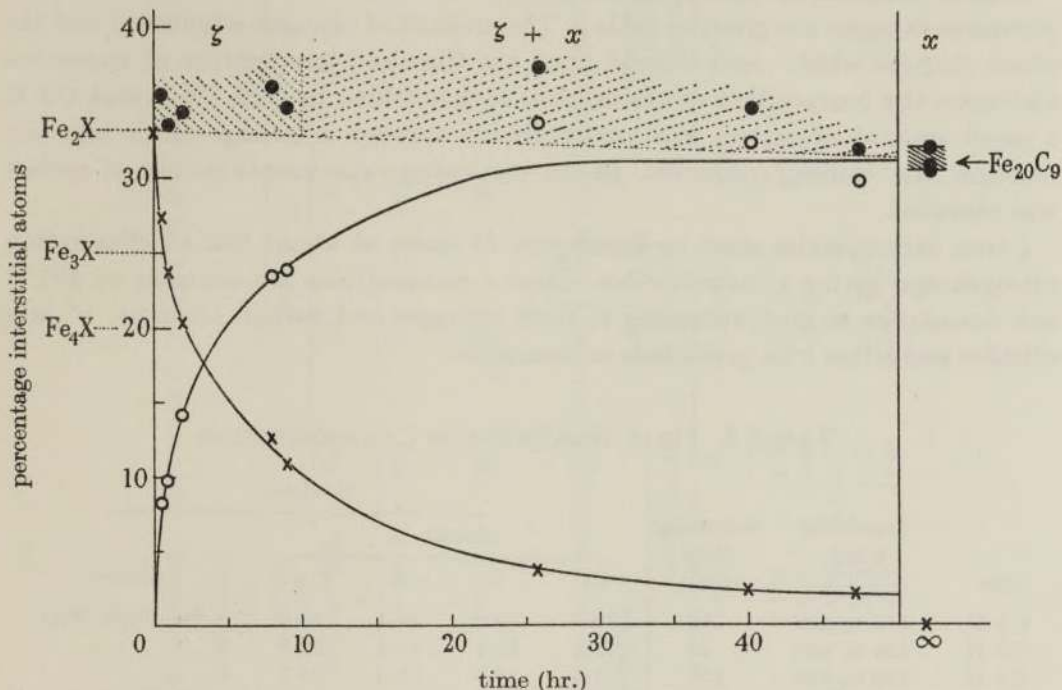


FIGURE 2. The reaction of carbon monoxide with ϵ -iron nitrides at 450°C . \times Nitrogen concentration, \circ carbon concentration, \bullet concentration of carbon plus nitrogen.

Photographs C6 to C8 show two phases, ζ and χ , with decreasing amounts of the ζ -phase and increasing amounts of the second phase χ , as the nitrogen concentration approaches zero. The phase χ was so designated because it was identified as the higher carbide of iron, the existence of which has previously been suspected and which has been known as 'X-carbide' (Hofmann 1928) or, erroneously, as ' Fe_2C ' (Bahr & Jessen 1933; Hägg 1934). This carbide, which it is proposed here should be named iron percarbide, is obtained homogeneous only by complete elimination of nitrogen and over a range of composition (30.4 to 32.3 atomic % C) which includes Fe_{20}C_9 (31.0 % C). A photograph (C8-H) of pure iron percarbide is included on plate 2 for comparison purposes.

The reaction of carbon monoxide with iron nitrides at 450 to 700°C (runs C9 to C14)

Table 2 shows that the end-product obtained by prolonged carburizing of γ -iron nitrides at 450 and 470°C is again iron percarbide. The intermediate carbonitrides show undistorted hexagonal structures. Since they are isomorphous with ϵ -phase iron nitrides, it is proposed here that they be named ϵ carbonitrides.

At 500° C the reaction of carbon monoxide with ϵ nitrides is more rapid than at 450° C, but, as at the lower temperature, results in the formation of percarbide when all nitrogen is eliminated. At 600° C, however, the product consists of a mixture of iron percarbide and cementite, while at 700° C only cementite and graphitic carbon are observed.

Heat treatment of ζ carbonitrides

Results obtained by annealing the products of runs C1 to C8 at different temperatures *in vacuo* are given in table 3. The amount of nitrogen eliminated and the phase changes which occur depend upon the time and temperature of treatment and upon the composition of the original carbonitride. In runs C4-H and C5-H a small amount of carbon was lost, probably through a leakage of air into the reaction tube causing oxidation. In the remaining experiments no loss of carbon was observed.

ζ -iron carbonitrides start to decompose *in vacuo* at about 350° C, eliminating nitrogen and giving ϵ carbonitrides. These ϵ carbonitrides are unstable at 450° C and decompose to give, according to their nitrogen and carbon contents, γ' or ϵ nitrides and either iron percarbide or cementite.

TABLE 3. HEAT TREATMENT OF ζ CARBONITRIDES

run	annealing temp. (° C)	annealing time (hr.)	product				phases
			atomic %				
			Fe	C	N	C+N	
C1-H	400 to 480	96	79.4	10.2	10.4	20.6	α -Fe, Fe ₄ N, Fe ₃ C
C2-H	400 to 420	40	73.1	11.1	15.8	26.9	ϵ
C3-H	380 to 420	120	71.3	15.7	13.0	28.7	ϵ
C4-H	450	65	71.3	23.8	4.9	28.7	χ , Fe ₃ C, (ϵ)
C5-H	450	70	78.3	20.0	1.7	21.7	α -Fe, Fe ₃ C, (ϵ)
C6-H	450	22	65.2	34.8	0	34.8	χ , Fe ₃ C, carbon
C7-H	420 to 440	72	66.7	33.3	0	33.3	χ , Fe ₃ C, carbon
C8-H	350	50	69.6	30.4	0	30.4	χ

The action of ammonia on iron carbides

When iron percarbide or cementite is nitrided by the action of ammonia at 450° C, the products are ϵ carbonitrides with a total interstitial atom concentration of about 33 %, which is probably near the upper homogeneity limit of the phase (see table 4 and photographs C9-N, C13-N). During reaction, carbon is possibly removed as methane although no proof of this was obtained.

The iron-carbon-nitrogen phase diagram

From results obtained by (i) carburizing nitrides, (ii) heat treatment of carbonitrides, and (iii) nitriding carbides, a ternary diagram, indicating probable phase fields of the iron-carbon-nitrogen system at 450° C and shown by figure 3, was constructed.

TABLE 4. REACTION OF AMMONIA WITH IRON CARBIDES AT 450° C

run	initial carbide or carbonitride		nitriding time (hr.) 450°	20 l./hr. NH ₃	atomic %			product	phases
	C	N			Fe	C	N		
C9-N (a)	26.2	4.5	2.3	χ, ε	—	—	—	—	ε, χ
C9-N (b)	26.2	4.5	5.5	χ, ε	66.7	—	7.3	25.9	ε, (ξ)
C13-N (a)	28.2	0	1.0	Fe ₃ C, χ	—	—	—	—	Fe ₃ C, χ, (ε)
C13-N (b)	28.2	0	4.0	Fe ₃ C, χ	—	—	—	—	ε, Fe ₃ C, χ
C13-N (c)	28.2	0	19.0	Fe ₃ C, χ	66.7	—	4.9	28.4	ε

TABLE 5. UNIT-CELL DIMENSIONS OF ε-IRON NITRIDES AND ε-IRON CARBONITRIDES

interstitial atomic %	unit-cell dimensions						replacement of N by C			
	nitrides		carbonitrides		run		% decrease			
	a	c	V	a	c	V	a	c	V	C/N
23.9	2.695	4.362	13.72	—	—	—	—	—	—	—
26.9	2.716	4.378	13.98	2.706	4.364	13.84	0.4	0.3	1.0	0.70
28.7	2.729	4.388	14.15	2.720	4.366	13.99	0.3	0.5	1.1	1.21
33.0	2.759	4.411	14.54	(2.749)	(4.392)	(14.37)	—	—	—	(1.00)
33.3	2.761	4.413	14.57	2.758	4.402	14.50	0.1	0.2	0.5	0.28
33.3	2.761	4.413	14.57	2.751	4.408	14.45	0.4	0.1	0.8	0.17

The mechanism of the reaction of carbon monoxide with iron nitrides

At temperatures at which carburizing gases react at an appreciable rate with α iron, the products are mainly free carbon and carbon dioxide (see Hofer 1944), and little carbide formation occurs. Penetration of carbon into the iron-atom lattice takes place readily only with the face-centred cubic lattice of γ iron, so that the carburizing of steel with carbon monoxide, methane or carbon is usually carried out at a temperature not lower than 900° C.

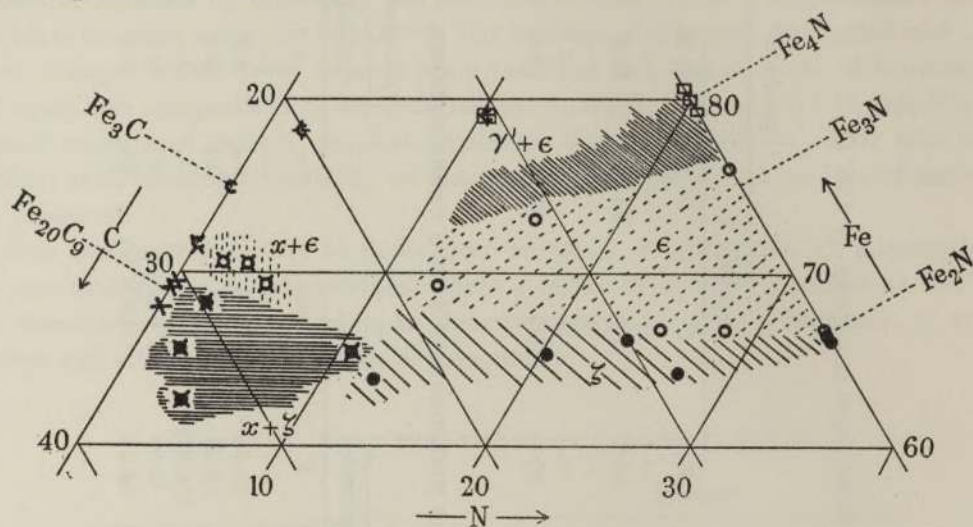
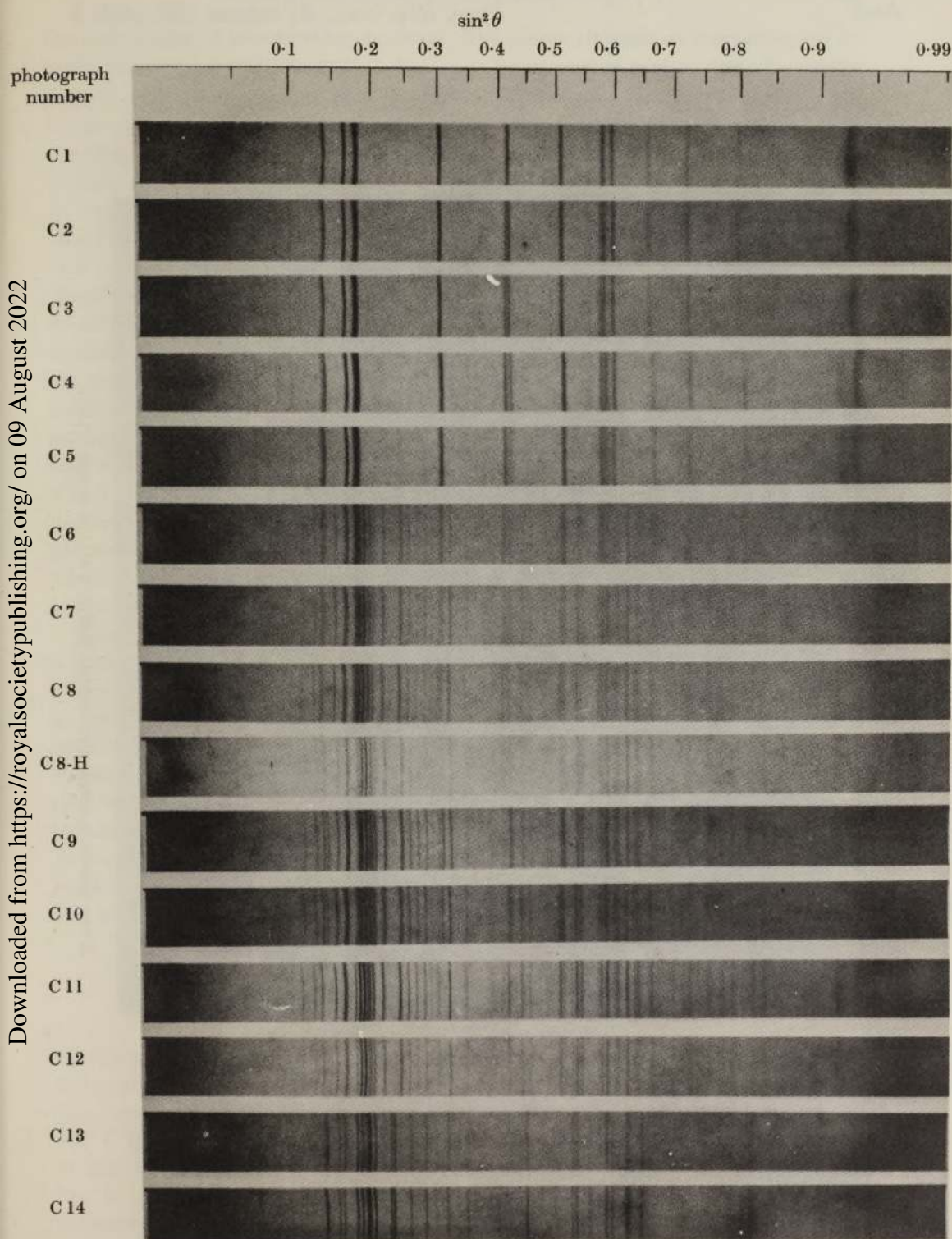


FIGURE 3. Part of the ternary diagram of the iron-carbon-nitrogen system at 450° C as deduced from present observations. + = α , \square = γ' , \circ = ϵ , \bullet = ζ , \times = χ , c = Fe_3C .

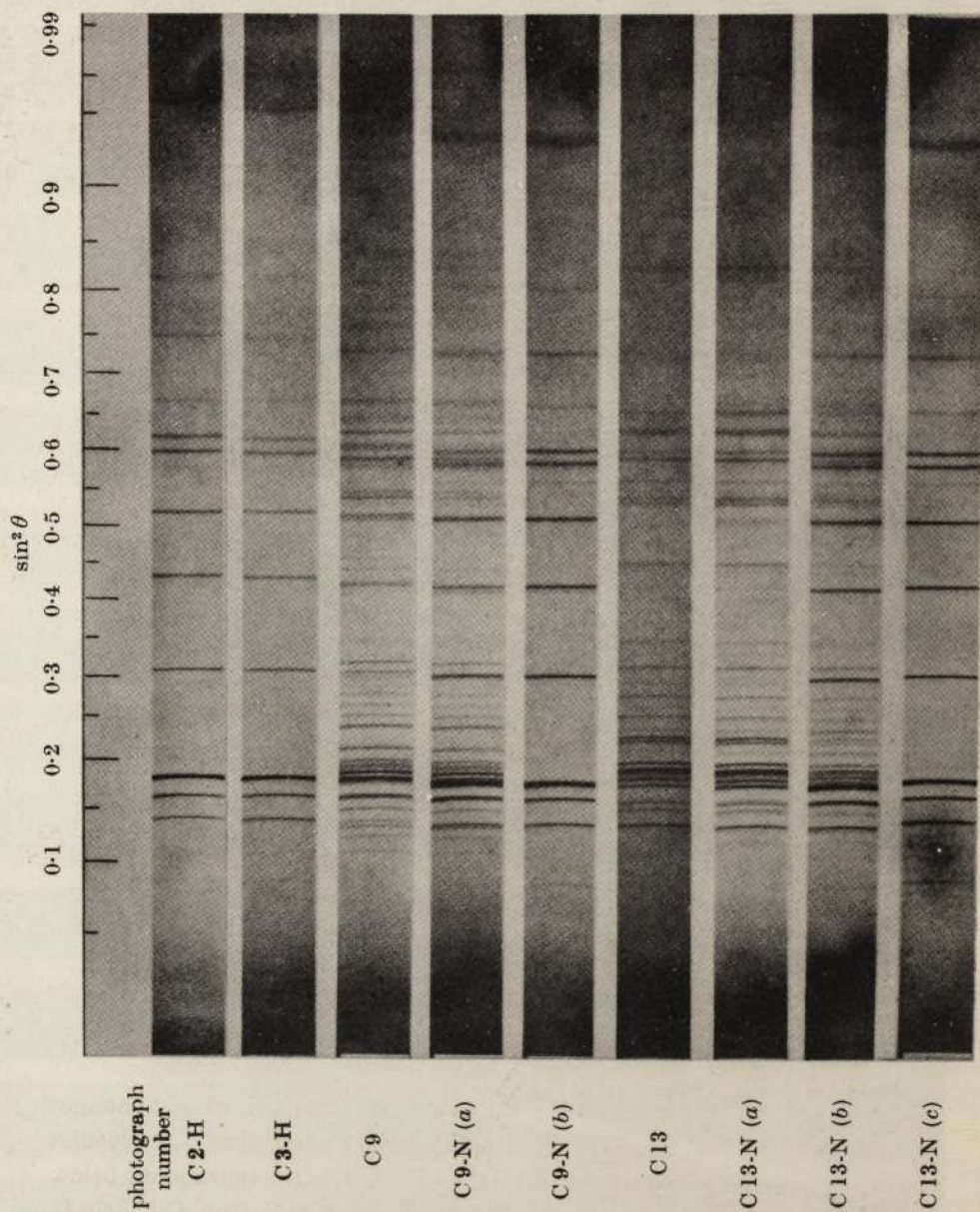
Nitrogen atoms derived from ammonia have much more power than carbon atoms to 'open up' the body-centred cubic α -iron lattice, which, with increasing nitrogen content, is converted first to an expanded face-centred cubic lattice (γ or γ' according to the temperature) and then to a more greatly expanded hexagonal close-packed structure (ϵ). In this respect, it may be significant that the maximum solubility of nitrogen in α iron (given by different workers as 0.13 weight % N at 590° C and 0.42 weight % N at 591° C) is certainly greater than that of carbon (0.035 weight % C at 725° C).

The interesting feature which arises from the present investigation is that once the α -iron lattice is expanded to either of the close-packed arrangements, carbon penetrates the structure at an appreciable rate, even at low temperatures, and replaces the nitrogen. Since this replacement is easily reversible, the affinities of carbon and nitrogen for iron must be of the same order of magnitude.

It appears that the nature of the reaction of carbon monoxide with iron nitrides is not the same at all temperatures. At 500° C or below, the only solid phase obtained by allowing the reaction to proceed to completion is iron percarbide. At 600° C a mixture of iron percarbide and cementite is obtained, while at 700° C cementite and graphitic carbon are observed. It is well known that free carbon, in addition to carbide, is formed when metallic iron is carburized with carbon monoxide at temperatures at which the present experiments were carried out (450 to 700° C). In



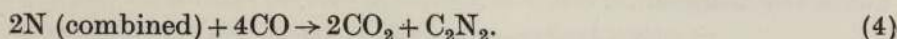
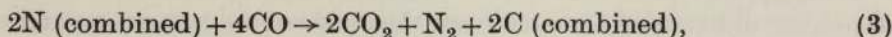
X-ray powder spectra of products C1, C2, C3, C4, C5, C6, C7,
C8, C8-H, C9, C10, C11, C12, C13 and C14.



X-ray powder spectra of products C 2-H, C 3-H, C 9-H and C 13-N.

the carburizing of iron nitrides, however, free carbon deposition was prevented at temperatures from 450 to 600° C, but only by removing carbon dioxide rapidly from the vicinity of the specimen. In several experiments, the results of which are not given in full, when the rate of gas circulation was decreased below a certain value, thereby causing a critical increase in the partial pressure of carbon dioxide, perceptible blackening of the surface of the specimen by graphitic carbon was observed. In two runs, where the concentration of carbon dioxide was allowed to increase steadily, the deposited carbon weighed very much more than the starting material. It is possible that, because of the rapidity of reaction, the concentration of carbon dioxide at 700° C was higher than the critical value, but although considerable carbon in addition to carbide was obtained at this temperature, the accelerated carbon formation is probably due not only to the presence of carbon dioxide, but also to the normal effect of temperature. According to Hofer (1944) carbon formation can continue until the iron is diluted to 1 % of the total iron-carbon mass, when the iron is then distributed in a finely divided state throughout the carbon. This suggests the intermediate formation of an unstable carbide, possibly iron percarbide or cementite, which decomposes by graphitization occurring inside the crystal lattice. It is unlikely that traces of carbon dioxide can directly catalyze free carbon formation at lower temperatures. It is, therefore, suggested that the presence of carbon dioxide allows a film of oxide to be formed on the iron surface, and it is this oxide which acts as the catalyst.

Apart from these observations there is, however, some quantitative evidence of a transition temperature in the reaction of carbon monoxide with iron nitrides. The volume of reacted carbon monoxide varies with time in the same general way as the carbon concentration of the solid phase (e.g. figure 2), but below 500° C is uniformly greater than the volume equivalent to the combined carbon. Since small amounts of polymerized cyanogen were observed in the inlet limb of the condensation traps of the apparatus, this apparent discrepancy is explained if nitrogen is eliminated from the nitride not only as molecular nitrogen but partly as cyanogen. In two experiments, analysis of the gas mixture in the circulating system after the reaction was complete showed only two constituents, carbon monoxide and nitrogen. The available evidence indicates, therefore, that two reactions occur:



On this assumption, and from the volume of carbon monoxide used, weight changes and analytical results, the proportion of eliminated nitrogen evolved as N₂ molecules was calculated. Excluding one anomalous result (run C 4), all experiments below 500° C (runs C 1 to C 11) gave values of 75 ± 6 %. At 500° C (run C 12) 86 % of the eliminated nitrogen, and at still higher temperatures (600° C, run C 13; 700° C, run C 14) all the eliminated nitrogen (100 ± 1 %) was evolved as N₂ molecules.

Only preliminary conclusions can be reached with respect to the mechanism by which carbon replaces nitrogen. Runs C 1 to C 8 are essentially replacement reactions,

and for these, figure 4 shows that there is an approximately linear relationship between the reciprocal of the nitrogen concentration (N) and the time (t). This indicates that the rate of replacement of nitrogen by carbon is given by a kinetic equation of the second order with respect to the interstitial nitrogen concentration. The reaction rate for an *individual* experiment could be followed from the carbon monoxide consumed. These data also conformed to a second order reaction. Therefore

$$-\frac{dN}{dt} \propto N^2,$$

or, since $N + C = a$, where C is the carbon concentration and a is approximately constant,

$$\frac{dC}{dt} = -\frac{dN}{dt} \propto (a - C)^2 \propto (a - C)N.$$

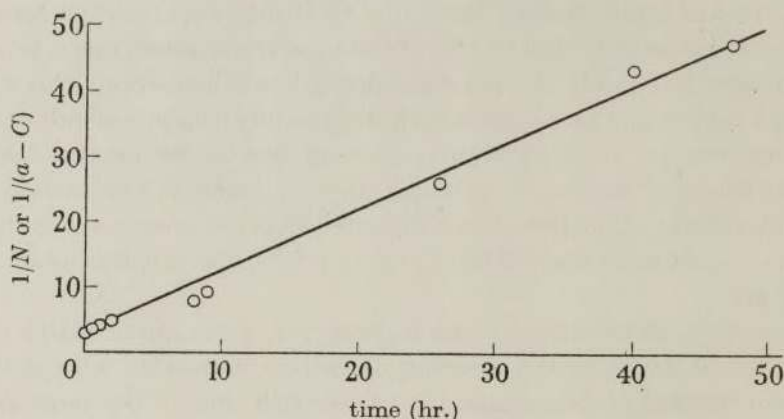
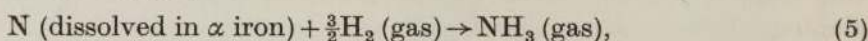


FIGURE 4. $1/N$ or $1/(a - C)$ plotted against time t , showing second-order reaction with respect to nitrogen concentration.

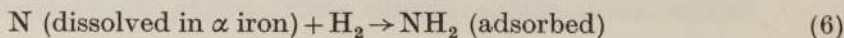
Engelhardt & Wagner (1932) have shown in the reaction



that

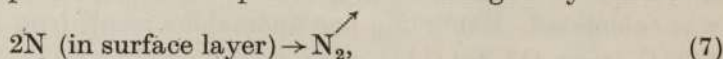
$$-\frac{dN}{dt} \propto p_{H_2}N,$$

where p_{H_2} is the partial pressure of hydrogen, and that the rate-determining process is not the diffusion of nitrogen from the inside of the iron-atom lattice to the surface, but is the reaction



occurring at the iron/gas interface.

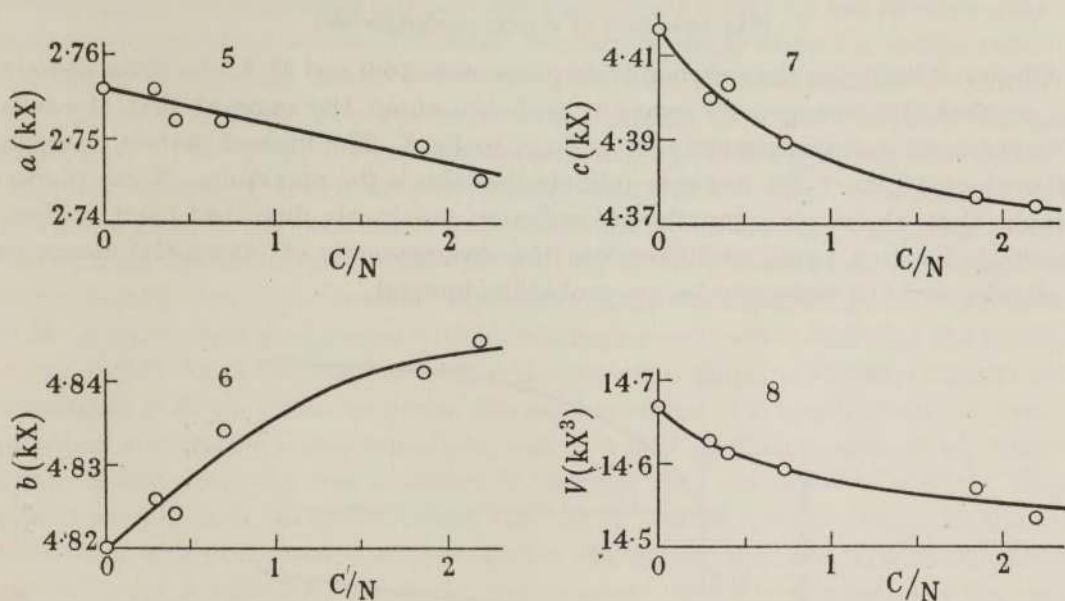
If the rate-determining process in the replacement of nitrogen by carbon is similarly



then the reaction rate would be given by the required second-order equation. The observation that the 3 : 1 ratio of nitrogen and cyanogen, formed at 450 and 470° C, is independent of time suggests, however, that nitrogen and cyanogen are products of simultaneous side reactions so that the complete reaction mechanism cannot be simple.

The structure of ζ -iron carbonitrides

The homogeneity limits of the ζ -carbonitride phase are approximately Fe_8N_4 and $\text{Fe}_8\text{C}_3\text{N}$. The total interstitial atom concentration ($\text{C} + \text{N}$) remains almost constant (found: 33.5 to 36.0 atomic %) as carbon replaces nitrogen. Values above 33.3 represent excess interstitial atoms above Fe_8X_4 . This is probably a real effect, but it may be due in part to analytical errors or to the presence of traces of free carbon. Near the limit $\text{Fe}_8\text{C}_3\text{N}$ (photograph C 5, plate 2), the positions of observed superlattice reflexions are identical with those on photographs of ζ nitride (part I) and the relative intensities of corresponding reflexions are the same, so that the positions of iron atoms and interstitial atoms in the two structures must be identical. With



FIGURES 5 to 8. Variation in unit-cell dimensions of ζ carbonitrides with increasing C/N ratio.

those carbonitrides containing less carbon (C1 to C4), and which were prepared by carburizing ϵ nitrides for shorter periods of time, it is found that the ϵ arrangement of interstitial atoms still partially persists. Thus, as carbon replaces nitrogen the prominent X-ray superlattice reflexion due to the ϵ arrangement of interstitial atoms (see part I) grows fainter on successive photographs C1 to C4, while those reflexions characteristic of the ζ arrangement gradually increase in intensity. At the same time, the anisotropic distortion of the iron-atom lattice, characteristic of the ϵ - to ζ -phase change, gradually increases. The expansion of the b axis of the unit cell, which occurs as the carbon/nitrogen ratio increases and which is shown by figure 6, is not, therefore, unexpected. Figures 5, 7 and 8, however, show that a , c and the volume of structure per iron atom V , all decrease with increasing carbon concentration, which suggests that in these carbonitrides the effective atomic radius of carbon (r_C) is smaller than that of nitrogen (r_N).

Comparing a ζ nitride with the ζ carbonitride C5, both having strictly isomorphous structures and each of which has an approximate composition Fe_2X , where X represents an interstitial atom, the following values are obtained (r_{Fe} is assumed = 1.260 kX):

	interstitial atomic %	C/N	Fe—X distances (kX)	r_{X}
ζ nitride	33.7	0	(4) 1.940 (2) 1.950	1.943 0.683
ζ carbonitride, C5	34.6	2.2	(4) 1.931 (2) 1.949	1.937 0.677

Thus, taking mean values, $r_{\text{N}} = 0.683$ and $r_{\text{C}} = 0.675 \text{ kX}$.

The structure of ϵ -iron carbonitrides

Observed limits for the ϵ -carbonitride phase were 26.9 and 33.3 interstitial atomic %, so that the homogeneity range is probably about the same as that of ϵ -iron nitrides, that is, approximately from Fe_3X to Fe_2X . The highest carbon/nitrogen ratio observed was 1.2/1, but it is unlikely that this is the maximum. X-ray photographs show the single ϵ -superlattice reflexion previously described (part I; Hendricks & Kosting 1930), and therefore the arrangements of interstitial atoms in ϵ nitrides and in ϵ carbonitrides are probably identical.

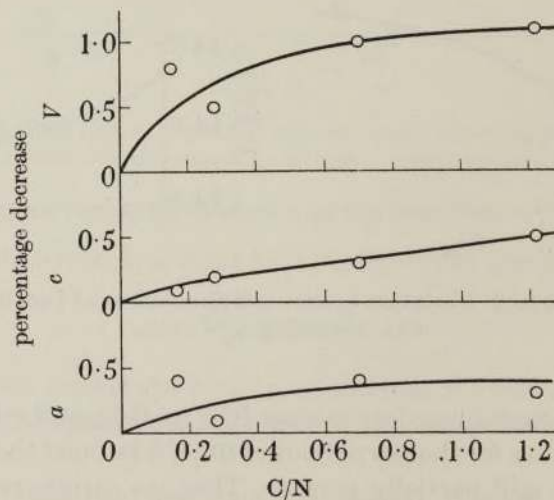


FIGURE 9. Decrease in unit-cell dimensions of ϵ carbonitrides with increasing C/N ratio.

To assess the effect on unit-cell dimensions of substituting nitrogen by carbon, each ϵ carbonitride was compared with a nitride of the same interstitial atom concentration (see table 5). Unit-cell dimensions for nitrides containing 26.9 and 28.7 atomic % N were calculated from the values for lower (Hägg 1929) and upper (the present investigation, part I) limits of the phase by linear interpolation. Although a and c are probably not strictly linear functions of the nitrogen concentration (Brunauer, Jefferson, Emmett & Hendricks 1931), the values so obtained agree very

closely with those given by Brunauer *et al.* and are sufficiently accurate for present purposes. It is shown in table 5 and graphically in figure 9 that the unit-cell dimensions decrease as carbon replaces nitrogen. The following results

	interstitial atomic %	C/N	Fe—X distance (kX)	r_x
ϵ nitride	33.0	0	1.937	0.677
ϵ carbonitride	33.0	1	1.930	0.670

give $r_N = 0.677$ and $r_C = 0.663$ kX.

DISCUSSION OF INTERSTITIAL STRUCTURES

According to Hägg's rules for the formation of interstitial alloys (Hägg 1931; see Evans 1946), the structures adopted are determined solely by the relative sizes of metal and non-metal atoms. 'Normal' structures result when the radius ratio of the atoms is less than about 0.59, and when this value is exceeded, 'complex' structures are formed. In accordance with this rule, iron nitrides have 'normal' structures, since $r_N/r_{Fe} = 0.56$, and cementite (Fe_3C), where $r_C/r_{Fe} = 0.61$, has a 'complex' structure. If values for the atomic radii of iron (1.26 kX), carbon (0.77 kX) and nitrogen (0.71 kX) are taken to be those upon which Hägg's generalization is based, then the mean radius ratio for Fe_8C_3N is 0.60, which is rather larger than might be expected for a 'normal' structure. Hägg argued that the effective radius of an interstitial atom increases with increasing concentration, and that the limiting value of 0.59 for a 'normal' structure is only valid if the interstitial atomic concentration is 50%. Since, however, the concentration of interstitial atoms (even if nitrogen is completely discounted) is greater in Fe_8C_3N than in cementite, it is not immediately clear why one structure is 'normal' and the other 'complex'. When actual atomic radii, as distinct from the '50%' values used by Hägg, in the two structures are compared, another major difference becomes apparent. Again, assuming $r_{Fe} = 1.260$ kX, the mean carbon-atom radius in cementite is the usual covalent value (Lipson & Petch 1940), whereas in the ζ carbonitride the mean atomic radii of carbon (0.675 kX) and nitrogen (0.683 kX) are much lower than the covalent radii of carbon (0.77 kX) and nitrogen (0.71 kX) atoms (Goldschmidt 1929; Neuburger 1936).

Another interesting feature of the present investigation is that in the 'normal' ϵ and ζ carbonitrides the effective atomic radius of carbon is less than that of nitrogen. A possibility is that the non-metal atoms lose electrons and occupy interstices as positive ions. These donated electrons may be absorbed in the 3-quantum shells of the iron atoms. It is not suggested that the interstitial atoms of all 'normal' structures exist as positive ions, but it may not be without significance that only those metals with an incomplete inner quantum shell form true interstitial alloys. Since carbon replaces nitrogen, within wide limits, without any marked structural change, it is perhaps a reasonable assumption that each carbon atom loses the same number of electrons (or the same fraction of an electron) as a nitrogen atom. The relative loss of electrons would thus be greater for carbon than for nitrogen and might account for the smaller effective atomic radius of carbon.

Values for the volume of structure per metal atom in the nitrides, the carbides and the carbonitrides of iron are in agreement with Hägg's observation (1931) that the metal atoms are packed more closely in 'complex' structures than in 'normal' structures.

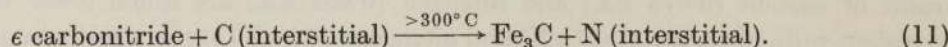
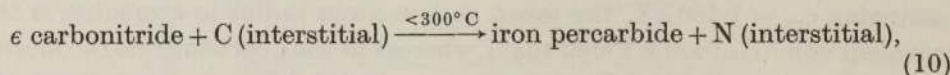
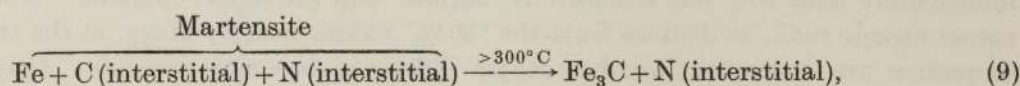
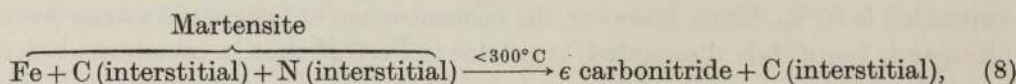
THE OCCURRENCE OF IRON CARBONITRIDES IN STEEL

Preliminary experiments carried out by Dr J. Mills, in collaboration with the present author, indicate that, in carburizing mild steel at 750° C with carbon monoxide, the penetration of carbon is greatly facilitated by previously nitriding the steel surface. Reactions similar to those described above occur. It also seems likely that carbonitrides are formed in the case-hardening of steel by the dry-cyaniding process.

Heidenreich, Sturkey & Woods (1946 *a, b*) report that when martensitic steel (C, 0.9; Si, 0.15; N, 0.0056 weight %) is tempered at 200° C, a fine dispersion of hexagonal Fe₃N, or some phase isomorphous with Fe₃N, is produced without any trace of the cementite which is normally obtained by similar treatment at temperatures above 300° C. This 'Fe₃N' is transformed to cementite at 350° C and thus may be identical with the so-called 'carbide' which Arbusow & Kurdjumow (1941) obtained by tempering martensite at 130 to 150° C.

Results of the present investigation indicate that the hexagonal phase reported as 'Fe₃N' is very probably an ϵ carbonitride. The unknown 'carbide' (Arbusow & Kurdjumow 1941) may be either a carbonitride or iron percarbide.

Possible reactions in the tempering of a martensite which contains nitrogen are



In a normal martensitic steel, tempered below 300° C, only small amounts of the carbonitride phase can be present, and thus most of the carbon must remain in the ferrite solution.

OTHER CARBONITRIDES

Additional experiments show that manganese, as well as iron, forms carbonitrides. Owing to the readiness with which manganese is oxidized, the reaction of carbon monoxide with η manganese nitride (Mn₃N₂) at 800° C gives manganous oxide (MnO) and carbon. The formation of oxide is prevented by carburizing with methane. In two runs at 750° C, products of the reaction of methane with Mn₃N₂ showed close-packed hexagonal structures and had interstitial atom concentrations near 25 %, of which more than half was carbon.

Further work on the carbonitrides of iron and manganese is proceeding.

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