CARBIDES, NITRIDES, AND CARBONITRIDES OF IRON

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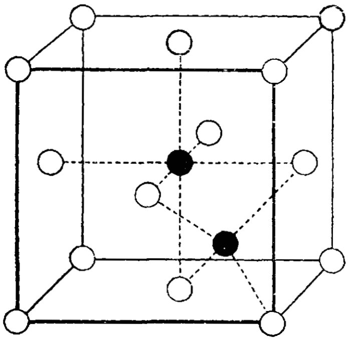
Introduction

Metallic interstitial solid solutions are alloys in which the solute atoms are situated in the interstices formed by the atoms of the metal solvent. Our knowledge of interstitial alloys is fragmentary, because those atoms which are small enough to occupy the interstices of a metal-atom lattice, *viz.*, hydrogen, boron, carbon, nitrogen, and, probably, also oxygen, have low scattering powers for X-rays and, in many cases, their location in the alloy is conjectural. Nevertheless, the results which the further study of these alloys is likely to yield are of importance in several fields : the elucidation of the finer features of their crystal structure will advance our fundamental knowledge of the metallic state ; they play an essential but obscure part as catalysts in such technically important reactions as ammonia synthesis and oxidation, the Fischer–Tropsch reaction, etc. ; and the interstitial carbides and nitrides are of importance in general ferrous metallurgy, and particularly in the case-hardening and heat treatment of steel.

The numerous interstitial solid solutions formed by the transition metals on the one hand, and hydrogen, boron, carbon, or nitrogen on the other, have been investigated in considerable detail by G. Hägg,[1] who has classified them on the basis of their crystal structures. Most of the transition metals have close-packed structures ; if we picture the metal atoms as rigid spheres, then the close-packed hexagonal structure can be regarded as being made up of triangularly close-packed layers of spheres, stacked in a close-packed sequence, *abababab*, the *a* layers being normally over each other, and similarly the *b* layers. The close-packed, face-centred structure similarly consists of close-packed layers, but these are stacked in an *abcabcabc* sequence. It is difficult to picture the interstices in such close-packed assemblages of rigid spheres ; that there are two different types of interstice can be seen from the figure, in which close-packed spheres are represented by the small hollow circles, and the centres of the interstices by the full circles. Hägg's classification is based on the metal-atom lattice (usually close-packed, each metal atom co-ordinated with twelve other metal atoms) and the type of interstice which is occupied, either tetrahedral (co-ordination number 4) or octahedral (co-ordination number 6). Interstitial alloys exist



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[1] *Z. physikal. Chem.*, 1929, *B*, **6**, 221 ; 1931, *B*, **12**, 33.

in which the metal atoms are not close-packed, but have body-centred or simple hexagonal structures. In both the close-packed structures there are two tetrahedral interstices and one octahedral, per metal atom. Not all the interstices need be occupied, but only one type of interstice, either tetrahedral or octahedral is occupied in a particular interstitial compound or intermediate phase. It is believed that in occupying an interstice the atom must be in contact with the surrounding metal atoms, a condition which limits the radius ratio of the atoms concerned. The condition for contact in the tetrahedral interstice is that the ratio of the radius of the interstitial atom, R_I, to that of the close-packed metal atom, R_M, shall be 0·22, and for an octahedral interstice, 0·41.

Interstitial carbides are of two kinds,[2] *viz.*, the refractory carbides such as those of titanium, zirconium, tantalum, etc. on the one hand, and carbides such as those of iron, cobalt, and nickel on the other. Carbides of the former group are chemically inert and melt only at exceedingly high temperatures. C. Agte and H. Alterthum [3] give the following melting points : ZrC, 3530° ; NbC, 3500° ; Mo_2C, 2690° ; MoC, 2690° ; HfC, 3890° ; TaC, 3880° ; W_2C, 2860° ; WC, 2870°. E. Friederich and L. Sittig [4] report the following melting points for corresponding nitrides : TiN, 2930° ; ZrN, 2930° ; VN, 2050° (decomposition) ; NbN, 2050° ; TaN, 2800° (decomposition) ; ScN, 2650°. Carbides of the second group are chemically reactive, being readily decomposed by dilute acids, and are only metastable at temperatures in the neighbourhood of 1000°. The corresponding nitrides are even less stable. Hägg has pointed out that inert carbides have the radius ratio, $R_I : R_M$, less than 0·59, whilst the ratio for the unstable carbides exceeds this value. Interstitial alloys are metallic in character, opaque, good conductors of heat and electricity, lustrous and, like metallic alloys, show variable composition ; in contrast to pure metals, however, the inert interstitial alloys melt only at exceedingly high temperatures. Their electrical conductivities decrease with rise of temperature. C. Agte and K. Moers [5] have described the preparation, in the pure state, and the properties, of a large number of high-melting carbides, nitrides, and borides ; using a filament technique, K. Moers has measured their electrical conductivities over a wide range of temperature ; the borides had the highest specific conductivities, even higher than those of the pure metals.

Atomic diffusion in solids can occur by two processes : where the diffusion involves the formation of primary substitutional solid solutions, an interchange of lattice sites by the participating atoms must take place ; where interstitial alloys are formed, the penetration of the smaller atoms from interstice to interstice in the lattice of the larger atoms is involved. The latter process probably involves a much smaller activation energy than the former. According to M. Paschke and A. Hauttmann [6] the rate of

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[2] See M. von Stackelberg, *ibid.*, 1934, *B*, **27**, 53 ; G. Hägg, *loc. cit.*, and A. Westgren, *J. Franklin Inst.*, 1931, **212**, 577.

[3] *Z. tech. Physik*, 1930, **11**, 182.

[4] *Z. anorg. Chem.*, 1925, **143**, 293.

[5] *Ibid.*, 1931, **198**, 233.

[6] *Arch. Eisenhüttenw.*, 1935—36, **9**, 305.

diffusion of manganese into iron at 1400° appears to be only about 1% of that of carbon.

The Reaction, $2CO = C + CO_2$

Metallic interstitial carbides are usually prepared by one or other of two methods : the interaction of elementary carbon with the metal or its oxide at high temperatures, or the interaction of a hydrocarbon gas or carbon monoxide with the metal or its oxide at much lower temperatures. The mechanism of the direct interaction of metal and carbon is obscure ; in some cases it undoubtedly involves the intermediate formation of a gaseous phase, carbon monoxide, hydrocarbon, or even metal vapour. The high temperature necessary when elementary carbon is employed, however, is undoubtedly connected with the high thermal stability of the graphite lattice. Because of its technical importance, the interaction of carbon monoxide with transitional metals and oxides, particularly with iron and its oxides, has been the subject of numerous investigations ; the literature concerning the cleavage of carbon monoxide, $2CO = C + CO_2$, $\Delta H = -39$ k.-cals., on metals of the iron group is extensive. There are, however, few papers dealing with the reaction in presence of other catalysts. G. Fester and G. Brude,[7] using palladium deposited on activated charcoal or activated silica, have observed some reaction at relatively low temperatures (240°). A. Foix[8] stated that, at $> 1100°$, carbon monoxide deposited amorphous carbon on diamond, the latter undergoing no change ; equilibrium had not been reached even after three hours. J. Cleminson and H. V. A. Briscoe[9] found that no reaction takes place below 400° when glass and mercury are the only contact surfaces ; they report, however, slow reaction at temperatures below 300° in the presence of solid carbon, magnesia, or alumina. A. R. McKinney[10] has investigated the decomposition of ethylene and carbon monoxide on metallic catalysts and concluded that decomposition of carbon monoxide is catalysed only by metals capable of forming carbonyls. R. L. Burwell (jun.) and H. S. Taylor[11] have shown that, when carbon monoxide is passed over zinc oxide at $> 184°$, the cleavage reaction occurs at the surface, and that the deposited carbon, presumably in the atomic form, is removed by hydrogen at the same temperature.

Finely divided iron, cobalt, and nickel and/or their oxides exceed greatly in catalytic activity all the above-mentioned solids, and there is little doubt that the formation of interstitial carbides plays an important, and probably essential, part in the catalytic mechanism. The activity of these iron-group metals and oxides varies over a wide range and is influenced greatly by the previous history of the catalyst. In spite of the large number of experimental studies, particularly of iron and its oxides, there is still disagreement as to the mechanism of the reaction. O. Boudouard[12] was of the opinion that the oxides of iron catalysed the deposition of carbon from carbon

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[7] *Ber.*, 1923, **56**, 2245.

[8] *Bull. Soc. chim.*, 1922, [iv], **33**, 678.

[9] *J.*, 1926, 2148 ; see also ref. (62).

[10] *J. Physical Chem.*, 1943, **47**, 152.

[11] *J. Amer. Chem. Soc.*, 1937, **59**, 697.

[12] *Compt. rend.*, 1899, **128**, 98, 307.

monoxide, whereas R. Schenck and F. Zimmerman[13] believed that the metal itself, and not its oxides, was the catalyst. S. Hilpert and T. Dieckmann[14] suggested, without experimental proof, that the iron itself is not the specific catalyst, but rather certain carbides, including a higher carbide, formed from the metal. It has been known for some time that, in the decomposition of carbon monoxide on iron or its oxides, carbide formation occurs.[15] W. Gluud, K. V. Otto, and H. Ritter[16] referred to the existence of a new carbide of iron, Fe_2C : when Fe_2O_3 was heated in carbon monoxide at 275°, rapid reduction to Fe_3O_4 occurred and was followed by the simultaneous deposition of carbon and formation of carbide ; the existence of Fe_2C was argued from the kinetic study of the reaction. U. Hofmann and E. Groll[17] obtained indications, from *X*-ray-diffraction photographs, of the existence of a new iron carbide mixed with the carbon deposited from carbon monoxide ; they supposed it to be the new carbide previously reported by Gluud and co-workers. About the same time F. Fischer and H. A. Bahr[18] reported indications of the formation of a higher carbide (Fe_3C_4) by the prolonged low-temperature (270°) interaction of carbon monoxide and ferric oxide. G. Hägg[19] found that the long continued treatment of iron or iron oxide with carbon monoxide at 225° gave a new carbide for which the formula Fe_2C was suggested ; the diffractions in its *X*-ray powder photograph were listed, but not analysed. H. A. Bahr and V. Jesson[19a] thought it probable that pure Fe_2C, containing 9·7% of carbon, could be prepared from iron and carbon monoxide by employing the lowest possible temperature of interaction, 225° or lower ; between 230° and 400° they concluded that, besides free carbon, a mixture of cementite and Fe_2C is formed, and over 400° only cementite, with 6·68% carbon. H. Tutiya[15] inferred from his own experimental results that iron itself functions not as the catalyst, but as a supporter of autocatalytic dissociation of carbon monoxide ; iron carbide is formed as soon as the iron comes in contact with the carbon monoxide, the two reactions,

$$3Fe + 2CO = Fe_3C + CO_2$$

and

$$2CO = C + CO_2$$

occurring simultaneously ; it is, so he states, the Fe_3C, which plays the chief part in the catalytic dissociation of carbon monoxide. Hofmann and Groll[17] claimed to have established with certainty that, when carbon is deposited from carbon monoxide, cementite is always present in the solid phase ; the formation of elementary carbon occurs, however, not by the decomposition of the cementite, for it was found that the latter, formed

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[13] *Ber.*, 1903, **36**, 1231 ; *Stahl u. Eisen*, 1905, **25**, 758.

[14] *Ber.*, 1915, **48**, 1281.

[15] K. Stammer, *Pogg. Ann.*, 1851, **82**, 136 ; I. L. Bell, *J.*, 1896, 209 ; A. Gautier and P. Clausmann, *Compt. rend.*, 1910, **151**, 16, 335 ; S. Hilpert and T. Dieckmann, *loc. cit.* ; H. Tutiya, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1929, **10**, 69.

[16] *Ber.*, 1929, **62**, 2483.

[17] *Z. anorg. Chem.*, 1930, **191**, 414.

[18] *Ges. Abh. Kennt. Kohle*, 1924/1927, **8**, 255.

[19] *Z. Krist.*, 1934, **89**, 92.

[19a] *Ber.*, 1933, **66**, 1238.

in this manner, could be heated in nitrogen for two hours at 450° without appreciable decomposition, whereas, when heated in carbon monoxide at the same temperature and for the same time, it deposited ten times its own weight of carbon. The *X*-ray diffraction diagrams of the higher carbide were obtained only from the products of experiments carried out below 400°, and it was therefore concluded that the higher carbide decomposed quickly at temperatures above 400°. Hofmann and Groll suggested that, when free carbon is formed by the interaction of carbon monoxide with iron or iron oxide, it is through the agency of the formation and decomposition of this higher carbide that free carbon and, in addition, iron and cementite are formed.

The following two well-established and significant experimental facts have an important bearing upon any theory claiming to describe the mechanism of this reaction. (i) The carbon formed from carbon monoxide is relatively highly graphitic; although microcrystalline, the crystallites present are much larger than those prepared by carbonising a carbonaceous solid at the same temperature;[20] whatever the reaction mechanism, therefore, it must involve a certain amount of mobility in the carbon atoms, in order that crystal growth may take place. (ii) The iron catalyst is dispersed in an extremely fine state throughout the whole of the deposited carbon, and the reaction continues until the concentration of iron in the carbon has been reduced to about 1%.[21] The iron is present in the carbon largely as carbide and is exceedingly difficult to remove; prolonged treatment with boiling hydrochloric and nitric acid is necessary for its elimination. The work of W. Rüdorff and collaborators[22] on the ferric chloride–graphite complex explains why attempts to eliminate this iron by treating the product with chlorine at high temperatures were only partly successful; under these conditions the ferric chloride formed would tend to become intercalated in the graphite crystal lattice. F. Fischer and H. A. Bahr[18] showed significantly, that, if an iron–copper catalyst interacts with carbon monoxide at 500°, the carbon formed contains highly dispersed copper in addition to iron, and this suggests that carbonyl formation is not responsible for the dispersion of the catalyst.

That the formation and decomposition of carbides or percarbides are not essential parts of the catalytic mechanism is indicated by the fact that the reaction can be carried out at high temperatures, at which cementite is unstable. According to H. A. Schwartz,[23] in high-purity iron–carbon alloys containing 0·03% of silicon the reaction, $Fe_3C \rightleftharpoons 3Fe + C$, proceeds to the right at all temperatures from 630° to the melting point of the eutectic. G. Naeser[24] states that the decomposition of cementite, which was followed by measurements of magnetic susceptibility, takes place at 1050—1060°. The

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[20] U. Hofmann, *Z. Elektrochem.*, 1936, **42**, 504.

[21] Cf., *e.g.*, von Wangenheim, *Ges. Abh. Kennt. Kohle*, 1924/1927, **8**, 227; F. Fischer and P. Dielthey, *Brennstoff-Chem.*, 1927, **8**, 388; 1928, **9**, 24; *Ges. Abh. Kennt. Kohle*, 1924/1927, **8**, 234.

[22] W. Rüdorff and H. Schulz, *Z. anorg. Chem.*, 1940, **245**, 121.

[23] *Trans. Amer. Soc. Met.*, 1935, **23**, 126.

[24] *Mitt. Kaiser Wilh. Inst. Eisenforsch.*, 1934, **16**, 211.

cementation of steel rods in a stream of pure carbon monoxide at temperatures up to 1000° has been investigated in detail by A. Bramley and A. J. Jinkins.[25] Under these conditions carbon atoms penetrate into the γ-iron lattice to form a solid solution (austenite), and cementite is formed only when the steel cools. This may take the form of inter-granular cementite and pearlite, according to the concentration of the carbon. It has been shown [26] that, if the cementation reaction is prolonged, even at temperatures as high as 1100°, considerable quantities of highly graphitic carbon containing dispersed iron are formed ; the iron is in the form of cementite, indicating that this reaction is essentially similar to that occurring at lower temperatures. Occasionally, the presence of the higher iron carbide mixed with excess of carbon was observed in samples which had been formed at temperatures as high as 900° ; however, the conditions necessary to bring about the formation of this carbide were critical and were not fully elucidated. Carbon is appreciably soluble in the face-centred cubic γ-iron, and the following appears a likely explanation of the reaction mechanism. Presumably the carbon monoxide molecules first condense on the surface of the steel [formation of a surface carbonyl (McKinney [10])], and two of the condensed molecules react to form a molecule of carbon dioxide (which is desorbed) and an adsorbed carbon atom (surface carbide) ; the carbon atom then penetrates, by way of the interstices, into the γ-iron lattice, leaving the surface free for the condensation of further carbon monoxide molecules. If a high concentration of carbon atoms in the iron is built up in this way, there will arise an increasing tendency for the formation of graphite crystals. How the first crystal nucleus is formed we do not know, but the diffusion experiments of Bramley and Jinkins [25] and others leave no doubt as to the relatively high mobility of carbon atoms dissolved in γ-iron. Evidence of this mobility is also apparent in partly graphitised alloys ; [27] photomicrographs show regions of carbon impoverishment immediately surrounding the graphite crystal flakes. During the carburisation of steel the highest concentration of carbon in the γ-iron will always occur in the surface layers, and it is therefore there that the formation of graphite crystals is most likely to occur. P. R. Marshall [28] carburised a small piece of steel to saturation in carbon monoxide at 1000° ; a photomicrograph of the product showed a relatively large graphite crystal immediately below the surface ; the crystal was surrounded by a eutectoid zone, which in turn was surrounded by a cementite network. Electron-microscope photographs of carbon monoxide-carbon [29] indicate that the iron impurity must be present in an extremely fine state of division. It appears probable, therefore, that the contamination of the elementary carbon by iron and cementite is due to the mechanical dispersion of the solid catalyst brought about by the graphite crystal-building forces acting

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[25] *Mem. Iron Steel Inst. Carnegie Schol.*, 1926, **15**, 17.

[26] J. Taylor and D. Laidler, unpublished.

[27] H. Carpenter and J. M. Robertson, " Metals ", Oxford University Press, London, 1939, vol. 2, p. 1172.

[28] Ph.D. Thesis, Univ. Durham, 1944, p. 82.

[29] *Ibid.*, p. 57.

in its surface layers.[30] A similar view has been advanced by L. J. E. Hofer [31] to explain the catalyst dispersion which occurs at much lower temperatures. If, however, we attempt to extend this view to explain the mechanism of the carbon-deposition reaction to lower temperatures, a difficulty arises, for carbon is only very sparingly soluble in the body-centred α-iron lattice. At 1130° γ-iron can dissolve 1·7% of carbon; at 725° this has fallen to 0·87%. At 725° the body-centred α-iron dissolves only 0·035% of carbon, which decreases to 0·007% at room temperature. Below the α–γ transition temperature, iron formed by the reduction of iron oxide will presumably be in the α-form, the penetration of carbon atoms into which would be expected to follow a somewhat different course from that obtaining in the case of γ-iron. Carbon monoxide does not react with massive iron at an appreciable velocity at temperatures below 750°. It might be supposed that the fine state of sub-division in which iron is formed by the reduction of oxide powder is responsible for the relatively high reaction velocities observed with some iron oxides in the temperature range 400—550°. The formation of cementite and iron percarbide, and the dispersion of the catalyst in the deposited carbon, in both the high- and low-temperature reactions, suggest that the reaction mechanisms are fundamentally similar. We shall return to this point later.

Iron Nitrides

Metallic iron does not react with molecular nitrogen, but, when the metal is heated in gaseous mixtures containing ammonia, it forms, at relatively low temperatures, a number of nitride phases. The interest in these nitrides was increased by the discovery by A. Fry,[32] that, when special steels containing aluminium and chromium (nitralloy) are heated in ammonia at 500°, hardening of the surface occurs without any further heat treatment. Case-hardening by nitriding is now carried out by subjecting the machined steel to the action of ammonia for seventy to ninety hours at 500—540°.

Various iron–nitrogen phases are formed by the progressive penetration of nitrogen into the iron lattice. The ammonia is dissociated at the iron surface, and nitrogen atoms from the adsorbed layer diffuse into the iron. At 500° the iron is in the α-form, the solubility of nitrogen in which is of the order of 0·3% at 500—540°. Above this concentration of nitrogen a second phase, γ', is formed; it has a face-centred cubic structure and is homogeneous for the range 5·7 to 6·1% of N; it is usually referred to as the nitride Fe_4N.[33] The next phase (ε) which appears as the nitrogen concentration increases has a close-packed hexagonal structure and a range of homogeneity of 7·3 to 11·1% of N; [34] this range includes the stoicheiometric formula Fe_3N (N, 7·72%). A phase still richer in nitrogen, the ζ-phase (Fe_2N contains 11·14% of N) also exists; it has a base-centred orthorhombic

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[30] See W. Baukloh and B. Edwin, *Arch. Eisenhüttenw.*, 1942, **16**, 197.

[31] *U.S. Bur. of Mines, Rep. Invest.* No. 3770, July, 1944.

[32] *Krupp Monatsh.*, 1923, **4**, 137; *Stahl u. Eisen*, 1923, **43**, 1271.

[33] G. Hägg, *Nova Acta Soc. Sci., Upsal.*, 1929, [iv], **7**, 1.

[34] G. Hägg, *loc. cit.*; A. Osawa and S. Iwaizumi, *Z. Krist.*, 1928, **69**, 26.

structure which can be formed by a slight distortion of the close-packed hexagonal structure of the ε-phase; it was first reported by G. Hägg.[35] Recently, K. H. Jack [36] has obtained evidence for the location of the nitrogen atoms in the γ'- and ζ-phases from the positions of super-lattice lines in their respective *X*-ray powder diffraction diagrams.

These iron nitride phases are formed successively as more and more nitrogen atoms penetrate into the interstices of the iron lattice; the nitriding reaction is reversed if the phases are heated in a vacuum or in an inert gas. The nitrides are dull grey powders which dissolve in dilute hydrochloric acid with the formation of ammonium chloride.

Because of the lower temperature at which it is carried out, nitriding is a slower process than carburising, and various attempts have been made to accelerate it; these have been critically reviewed by E. Kunze,[37] who states that phosphatising before nitriding is the only method of increasing both the depth of penetration and the concentration of nitrogen at the surface of the steel. H. Bennek and O. Rüdiger [38] have studied the nitriding of steel in a glow discharge in nitrogen, and have reported greater hardness and a slightly deeper case than were obtained in the normal nitriding process. The difference in the stability of nitrides and carbides is probably not unconnected with the diatomic character of elementary nitrogen and the polyatomic character of elementary carbon.

Carbonitrides

In addition to carburising and nitriding, steel can also be case-hardened by immersion in a bath of molten sodium cyanide.[39] A bath made up of sodium cyanide 30—45%, sodium carbonate 40—37%, and sodium chloride 30—18% is maintained at about 870°, and both carbon and nitrogen atoms penetrate into steel immersed in the molten mixture. There is no reason to believe that the carbon and nitrogen penetrate into the steel as cyanide ions, as these would tend to form an ionic lattice with the iron; it is probable that they penetrate as individual atoms forming a metallic interstitial alloy by simultaneously occupying different interstices. Still another process of case-hardening, termed " dry cyaniding " or " carbonitriding " has been developed recently [40]; this consists in heating the steel in an atmosphere (H_2, 40; CO, 20; and N_2, 20%) to which controlled amounts of ammonia and methane have been added. It is carried out at a temperature somewhat lower than that used in carburising and, it is claimed, produces a case which is deeper and of greater wear-resistance than a carbide case. Presumably both carbon atoms from the methane, and nitrogen atoms from the ammonia, penetrate into the steel and simultaneously occupy different interstices. Until recently little fundamental knowledge of ternary interstitial solid solutions of this kind was available.

G. J. Fowler [41] reported that, when carbon monoxide was passed over

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[35] *Nature*, 1928, **122**, 962: *Nova Acta Soc. Sci., Upsal.*, 1929, [iv], **7**, 1.

[36] *Proc. Roy. Soc.*, 1948, *A*, **195**, 34.

[37] *Arch. Eisenhüttenw.*, 1944, **18**, 57.

[38] *Ibid.*, p. 61.

[39] H. Carpenter and J. M. Robertson, *op. cit.*, p. 1123.

[40] W. H. Holcroft, *Metal Progr.*, 1947, **52**, 380.

[41] *J.*, 1901, **79**, 285.

iron nitride (Fe_2N), carbon dioxide, but no cyanogen, was formed; this result indicated that the carbon deposition reaction, $2CO = C + CO_2$, took place on the surface of the nitride. A. Fry[32] suggested the possibility of the existence of carbonitrides. A. Bramley[42] studied the simultaneous diffusion of carbon and nitrogen into steel by carrying out gaseous cementations in the vapours of pyridine and methyl cyanide; he found that nitrogen diffuses into steel in much the same manner as carbon. W. Köster[43] has studied the properties of iron supersaturated with both carbon and nitrogen, with particular reference to theories of age-hardening.

Several carbides take up nitrogen to form complex compounds containing both carbon and nitrogen. Unless nitrogen is rigorously excluded in the preparation of alkaline-earth carbides, carbon–nitrogen complexes are formed. According to T. Aono,[44] with calcium the cyanide is first formed; it then decomposes to form the cyanamide and free carbon. C. H. Prescott, jun., and W. B. Hincke[45] studied the interaction of aluminium nitride and solid carbon in the temperature range 1774—1909° K.:

$$4AlN + 3C = Al_4C_3 + 2N_2$$

M. von Stackelberg, E. Schnorrenberg, R. Paulus, and K. F. Spiess[46] found that, in the presence of excess of nitrogen, aluminium and carbon interact at 1800° to form the compound Al_5C_3N, the appearance and properties of which scarcely differ from those of the carbide Al_4C_3; they consider that this carbonitride is an intermediate stage in the complete nitriding of the carbide,

$$5Al_4C_3 + 10N_2 = 4Al_5C_3N + 3C + 8N_2 = 20AlN + 15C$$

M. von Stackelberg and K. F. Spiess[47] investigated the crystal structure of this carbonitride by *X*-ray diffraction; they suggested that the lattice consists of five planes of aluminium atoms arranged hexagonally with three planes of carbon atoms and one plane of nitrogen atoms alternately between them. This view is speculative; the crystallographic similarity of nitrogen and carbon atoms suggests that a more random distribution of these atoms would obtain.

In the ternary system, titanium–carbon–nitrogen, compounds are formed, usually termed titanium cyanonitrides, which are highly refractory and show an intense metallic lustre. Well-developed, copper-coloured, cubic crystals of this material are sometimes found in blast furnaces which have been smelting titaniferous iron ores. The substance has also been reported in meteorites. F. A. Bannister[48] has examined, by *X*-rays, specimens of both meteoric and terrestrial origin and confirmed that they are alloys of titanium, carbon, and nitrogen; he concluded, however, that there is, as yet, insufficient evidence to prove the existence of a complete series of

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[42] *Mem. Iron Steel Inst. Carnegie Schol.*, 1926, **15**, 174.

[43] *Z. Metallk.*, 1930, **22**, 289; *Arch. Eisenhüttenw.*, 1929—30, **3**, 553, 637; *Stahl u. Eisen*, 1930, **50**, 254, 629.

[44] *Bull. Chem. Soc. Japan*, 1941, **16**, 91, 106.

[45] *J. Amer. Chem. Soc.*, 1928, **50**, 3228.

[46] *Z. physikal. Chem.*, 1935, **175**, 127.

[47] *Ibid.*, p. 140.

[48] *Min. Mag.* 1941, **26**, 36.

mixed crystals. C. Agte and K. Moers[5] have shown, by X-ray diffraction, the existence of mixed crystals in the systems TiC–TiN and TaC–TaN. H. Ste.-C. Deville[49] claimed to have prepared niobium carbonitride by heating Nb_2O_5 with sodium carbonate at 1200° in a graphite crucible; he gave it the formula mNbN,nNbC. By a similar method of preparation A. Jolly[50] obtained the same product and stated that he obtained niobium oxycarbonitride by heating the pentoxide with ammonium cyanide in a graphite crucible.

O. Heusler[51] reported that, when uranium carbide, UC_2, was heated in nitrogen at 1100°, it was eventually converted into nitride; at higher temperatures (1500°) mixtures of carbide and nitride were formed. The characterisation of compounds of this type, without the use of X-ray-diffraction methods, is unsatisfactory, and it is possible that carbonitride phases were formed in these reactions.

The above evidence suggests the close crystallographic similarity of carbon and nitrogen atoms, and the possibility of the existence of a large number of hitherto unknown compounds and intermediate phases, interstitial, ionic and covalent, containing both carbon and nitrogen. The existence of nitrogenous carbons[52] is further evidence of this similarity; in fact, the replacement of carbon by nitrogen, or *vice versa*, may occur in any crystal in which electronic compensation is possible.

A detailed study of the formation and properties of iron carbonitrides has been carried out by K. H. Jack.[53] Pure carbon monoxide was circulated over iron nitride powders, heated at various temperatures (450°, 470°, 500°, and 600°). The reaction, $2CO \rightarrow CO_2 + C_{(atomic)}$, occurred at the surface of the nitride; at the lower temperatures there was, apparently, little tendency for the formation of graphitic carbon, suggesting that the presence of nitrogen atoms in the interstices of the iron atom lattice tends to inhibit this reaction, and thus lending support to the view advanced above that carbon formation is not a surface reaction but occurs within the iron lattice. The iron ε-nitrides, containing 31—33 atom-% of nitrogen, treated in this manner at 450°, gradually lost nitrogen and gained carbon at approximately the same rate; the solid phase remained homogeneous until about three-quarters of the nitrogen atoms originally present had been replaced by carbon atoms. Throughout this interchange the structure of the solid phase remained similar to that of the parent ε-nitride; its iron-atom lattice showed the base-centred orthorhombic structure of the ζ-nitride. As the interaction with carbon monoxide was continued beyond the above stage, a second solid phase appeared; this proved to be an iron percarbide, which was obtained in the pure state when all the nitrogen had been eliminated from the iron nitride.

The percarbide has a small range of composition (30·4—32·4 atom-% of carbon) which includes $Fe_{20}C_9$ (C, 31·0%). Although this percarbide is probably identical with that reported by previous workers (see above),

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[49] *Compt. rend.*, 1868, **66**, 183.

[50] *Bull. Soc. chim.*, 1868, [ii], **25**, 506.

[51] *Z. anorg. Chem.*, 1926, **154**, 333.

[52] H.L. Riley, *Quart. Reviews*, 1947, **1**, 63.

[53] *Proc. Roy. Soc.*, 1948, *A*, **195**, 41.

Jack was the first to prepare this compound in a pure state, free from elementary carbon, iron, and cementite. He has suggested [54] that it has either an orthorhombic or a hexagonal crystal structure. The γ'-iron nitrides also interacted with carbon monoxide at 450° and 470°, and were finally converted into the pure iron percarbide ; in these experiments, however, the intermediate homogeneous carbonitride phase showed the ε-iron nitride hexagonal structure. At 600° the ε-iron nitrides reacted with carbon monoxide, to give finally a mixture of iron percarbide and cementite, and at 700° only cementite and graphitic carbon could be detected. The ζ-iron carbonitrides decomposed in a vacuum at about 350°, yielding ε-carbonitrides which decomposed further at 450° to form γ'- or ε-nitrides and iron percarbide or cementite, according to the initial composition of the carbonitride. Iron percarbide or cementite heated in ammonia at 450° yielded ε-carbonitride phases.

During the interaction of the iron nitrides with carbon monoxide at 450°, a proportion of the nitrogen was eliminated from the solid phase as cyanogen, and the remainder as elementary nitrogen.

The variation of the lattice dimensions as interstitial nitrogen is replaced by interstitial carbon in the homogeneous phases is of considerable interest and importance. The carbon atoms in the ζ-carbonitrides almost certainly occupy the position vacated by the nitrogen atoms in the parent nitride ; this is suggested by the position of the superlattice lines in the respective X-ray powder diffraction diagrams. The anisotropic distortion of the iron-atom lattice, which is characteristic of the formation of the ζ-nitride from the ε-nitride, shows an interesting modification in the analogous carbonitride conversion. As the ratio of carbon to nitrogen increases in the carbonitride phases, a slight expansion of the lattice along the b-axis occurs ; there is, however, a progressive decrease along the a and c axes, which results in an overall decrease in volume. This result indicates that in these carbonitrides, the atomic volume of the carbon is less than that of the nitrogen. Assuming the radius of the iron atom, R_{Fe}, to be 1·260 kX, Jack finds the radii of the nitrogen atom, R_N, and the carbon atom, R_C, to be, respectively, 0·677 and 0·663 kX, in the ε-phases. These values are substantially smaller than the covalent radii of carbon (0·771) and nitrogen (0·70) atoms.[55] H. Lipson and N. J. Petch [56] have attempted to locate the positions of the carbon atoms in cementite and given the following values as the Fe–C distances : 2·15(2), 2·06(2), 1·89, and 1·85 kX, *i.e.*, an average of 2·03 kX which Lipson and Petch consider has more significance than any of the separate values. Taking 1·260 kX as the radius of the iron atom, the average gives 0·770 kX as the radius of the carbon atom, *i.e.*, a value identical with the covalent radius. If, however, the smaller Fe–C distances are significant, then values of R_C even less than those reported by Jack are indicated. Jack's values for R_C and R_N, and also the fact that he finds $R_N > R_C$ in these alloys, are consistent with the view that the carbon and nitrogen are present in the

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[54] *Proc. Roy. Soc.*, 1948, *A.*, **195**, 56.

[55] L. Pauling, " Nature of the Chemical Bond ", Cornell Univ. Press, 1944, p. 164.

[56] *J. Iron and Steel Inst.*, 1940, **142**, 95.

interstices, not as neutral or negatively charged atoms, but as positive ions, and that they have lost electrons either to the incomplete 3*d* level in the iron atom or to an incompletely filled band in the alloy crystal. The higher electronegativity of nitrogen compared with carbon suggests that this transfer of electrons will occur less readily, and therefore to a smaller extent, with nitrogen than with carbon, which may account for the smaller observed value of R_C. The above value of R_C gives a radius ratio $R_C : R_{Fe}$ of 0·54, which is distinctly less than Hägg's critical value of 0·59. W. Seith and O. Kubaschewski [57] have shown that carbon in a steel wire heated to 1000° and under a potential gradient diffuses towards the cathode much more rapidly than towards the anode, a result in keeping with the above views.

Conclusion

The covalent radius of the boron atom is 0·88 *kX* ; its smaller electronegativity, however, may bring about a loss of electrons, and consequently a smaller effective radius in an interstitial alloy ; in this respect, the high electronic conductivity of interstitial borides, reported by Moers,[5] is suggestive. The existence of borocarbides, boronitrides, and perhaps borocarbonitrides appears possible. The position of oxygen is also of interest ; its covalent radius is 0·66 *kX*, *i.e.*, less than those of carbon and nitrogen. Its electronegativity is, however, much greater and the tendency will therefore be for it to form an ionic lattice rather than an interstitial alloy. Nevertheless, it has been suggested [58] that solid solutions of ferrous oxide in metallic iron exist. R. Schenck [59] has gone further and postulated the existence of oxoaustenite, a solid solution of carbon and oxygen in iron in equilibrium with a $CO-CO_2$ atmosphere. H. Dünwald and C. Wagner,[60] however, from a study of the $CO-CO_2$ equilibrium over carbon dissolved in iron, found that at 800° α- and γ-iron can co-exist in equilibrium and that the concentration of carbon in the α-phase is about 0·025% ; they calculate that the solubility of oxygen in α-iron at 800° or in γ-iron at 1000° is less than 0·01%. It has been shown [61] that preliminary surface oxidation or nitriding of a steel specimen increases the velocity of its carburisation in carbon monoxide. This may be due merely to the "opening up" of the surface. The carbonitride results, however, suggest that the increase in velocity may be due to the initial presence of oxygen or nitrogen atoms in the interstices of the iron lattice, facilitating the entry of carbon atoms. If this is so, then an explanation of the catalytic activity of certain iron oxides in the deposition of carbon is suggested : during the progressive reduction of the oxide by carbon monoxide a stage will be reached at which residual interstitial oxygen will probably still be present in the newly-formed iron lattice, and this residual oxygen possibly facilitates the entry of carbon atoms.

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[57] *Z. Elektrochem.*, 1935, **41**, 551.

[58] A. Matsubara, *Z. anorg. Chem.*, 1922, **124**, 42 ; E. D. Eastman and R. M. Evans, *J. Amer. Chem. Soc.*, 1924, **46**, 892.

[59] *Z. anorg. Chem.*, 1927, **167**, 254, 315.

[60] *Ibid.*, 1931, **199**, 321.

[61] H. L. Riley's co-workers, unpublished.

The deposition of carbon from carbon monoxide is highly susceptible to catalytic influences ; *e.g.*, W. Bauklok and G. Henke [62] have shown that the deposition can be decreased by as much as 95% by the addition of 1% of ammonia, cyanogen, or hydrogen sulphide ; it appears possible that interstitial phenomena are concerned in these inhibitions. The dispersion of the metal catalyst in deposited carbon, the pitting of platinum catalysts in ammonia oxidation, and the use of metal catalysts in reactions involving hydrogen, all point to the importance of interstitial reactions in catalysis. S. Weller, L. J. E. Hofer, and R. B. Anderson [63] concluded that *bulk* cobalt carbide is neither an intermediate nor a catalytically active substrate in the Fischer–Tropsch synthesis.

The interaction of carbon monoxide with iron nitrides suggests similar reactions with other metal nitrides and the existence of a large number of new carbonitride phases. These possibilities are being investigated.

Apart from the technical interest of the above carbonitride phases in the heat treatment and case hardening of steel, their detailed crystallographic study offers a new approach to the investigation of the metallic state. The quantum theory of solids has not yet been applied to interstitial alloys, but there is little doubt that accurate data, such as that given in K. H. Jack's papers, will open up this field. It is significant that both interstitial carbon and nitrogen have a great effect upon the α–γ change point of iron ; it therefore appears possible that the measurements of the electronic specific heats [64] of carbides, nitrides, and carbonitrides would yield further valuable results.

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[62] *Metallwirt.*, 1940, **19**, 463.

[63] *J. Amer. Chem. Soc.*, 1948, **70**, 799.

[64] See F. Seitz, " The Modern Theory of Solids ", McGraw-Hill, New York, 1940, p. 487.