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## Development and Current Status of Gaseous Nitrocarburizing

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### ABSTRACT

Physical metallurgy aspects of gaseous ferritic nitrocarburising are reviewed in the light of basic studies undertaken since 1975 which have illustrated inconsistencies between the iron-carbon-nitrogen ternary phase diagram at 570°C and the experimental observation of the co-existence of the  $\epsilon$  carbonitride phase and ferrite. Thermodynamic investigations by Xu and Li<sup>(4)</sup> together with those by Slycke et al<sup>(5)</sup> are reviewed to illustrate compatibility between a modified isothermal section of the Fe-C-N system and the formation and growth of a monophasic  $\epsilon$  structure under a variety of processing conditions. The implications of the modified diagram in terms of innovations in industrial ferritic nitrocarburising practice are discussed, together with limitations on the control of the process. The importance of the developing technology of black nitrocarburising for enhanced wear, fatigue, and corrosion resistance is emphasised. Basic studies and industrial status of austenitic nitrocarburising treatments are also reviewed, which highlight the importance of substrate strengthening for high load bearing applications of anti-scuff thermochemical treatments.

### INTRODUCTION

Ferritic nitrocarburising processes are those thermochemical treatments which involve the diffusional addition of both nitrogen and carbon to the surface of ferrous materials at temperatures completely within the ferrite phase field<sup>(1,2)</sup>. The primary object of such treatments is usually to improve the anti-scuffing characteristics of ferrous engineering components by producing a "compound layer" on the surface which has good tribological properties, Fig.1. In addition, the fatigue characteristics of the material can be considerably improved, particularly when nitrogen is retained in solid solution in the "diffusion zone" beneath the compound layer. This is normally achieved by quench-

ing into oil or water from the treatment temperature, usually 570°C.

Nitrocarburising treatments were first introduced about forty years ago; since that time an extremely wide range of engineering components, such as rocker-arm spacers, textile machinery gears, pump cylinder blocks and jet nozzles, have been treated for wear resistance, while components such as crankshafts and drive shafts have been treated for improved fatigue properties.

Ferritic nitrocarburising treatments have been successfully applied to most ferrous materials, including wrought and sintered plain carbon and alloy steels, stainless steels and case irons. However, the most marked improvement in both anti-scuffing and fatigue properties, relative to



**Fig. 1.** Mild steel after three hour gaseous nitrocarburising in an ammonia/endermotic gas mixture at 570° followed by oil quenching<sup>2)</sup>.

untreated material, is found with plain low-carbon steels.

Until late 1960's, the only nitrocarburising processes available used a medium of molten cyanide-based salts to confer the property improvements required. However, since then concern about the overall environmental aspects of heat treatment processing with cyanide-based salts has been increasing. Consequently, there has been intense interest in the development of cyanide-free nitrocarburising treatments as technically and economically viable alternatives to the cyanide-based processes.

Considerable progress has been made over the last twenty-five years in the development of essentially toxic free salt bath nitrocarburising treatments and more recently environmentally harmless plasma methods. However, it is the purpose of the present paper to review only those scientific and technological studies which have led to both the widespread introduction and greater appreciation of gaseous nitrocarburising treatments.

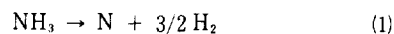
### PHYSICAL METALLURGY ASPECTS OF GASEOUS FERRITIC NITROCARBURISING

A particularly important and detailed study into the scientific understanding of gaseous nitrocarburising treatment was published by Prenosil in 1965<sup>3)</sup>. He investigated the structure and composition of the compound layer formed on relatively pure iron after a gaseous nitrocarburising treatment at 580°C in

atmospheres containing approximately 50% ammonia and 50% propane. In this investigation, it was reported that the presence of a high carbon content, in what otherwise would be a simple epsilon nitride compound layer, considerably improved its hardness and wear resistance. These observations have recently been confirmed in more detailed structural studies<sup>4)</sup>. Earlier work by Prenosil had shown that conventional nitriding atmospheres with a high dew point led to the presence of oxygen in the epsilon phase. This oxygen content was found to increase with increasing partial pressure of oxygen and it was further indicated that a similar saturation of the epsilon carbonitride phase was to be expected. Although the catalytic effect of oxygen on the rate of absorption of nitrogen into the surface of iron had been reported as early as 1935 by Bramley<sup>5)</sup>, the significance of oxygen in gaseous nitriding treatments was not really appreciated until it was investigated in detail by Eckstein and Lerche in 1968<sup>7)</sup>, who showed that it increased the rate of epsilon nitride formation. On the basis of this evidence it was concluded by Bell<sup>6)</sup> that oxygen should also increase the rate of epsilon carbonitride formation.

The nitrogen, carbon and oxygen activities of the nitrocarburising atmosphere necessary to achieve the desired oxygen-bearing epsilon carbonitride layer have recently been evaluated scientifically for a range of commercial steels by Slycke and Sproge<sup>8)</sup>. The basic consideration behind all gaseous nitrocarburising processes is the type of atmosphere which can be used to cause carbon and nitrogen to be added simultaneously to the surface of ferrous materials and so produce the desired epsilon phase. The compositions and activity relations of various types of typical industrial nitrocarburising atmospheres in quasi equilibrium are shown in Table and are based on data derived from an unpublished mathematical model by Slycke<sup>9)</sup>.

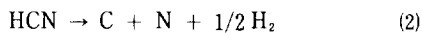
Ammonia is the most readily available source of active nitrogen and at 570°C dissociates on ferrous surfaces according to the following reaction:



and the nitriding activity is given by the expression :

$$a_N^* = K_1 \frac{p\text{NH}_3}{p\text{H}_2^{3/2}}$$

In addition, there are small levels of hydrogen cyanide in the furnace atmosphere present as a result of ammonia interaction with carbon monoxide. This has been shown recently by Slycke and Sprøge<sup>8)</sup> to supply nitrogen in parallel to reaction (1) as follows :

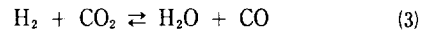


$$a_N^{**} = K_2 \frac{p\text{HCN}}{a_c p\text{H}_2^{1/2}}$$

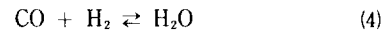
and is now regarded as the principle source for the mass transfer of nitrogen in the rapid build up of the compound layer. In practice the nitrogen activity of endogas based atmospheres tends to be lower than shown in Table 1, while it can be seen from Table 1 that the nitrogen activity of mixed atmospheres can be easily varied by, for example, additions of hydrogen.

The contents of carbon and oxygen bearing

constituents of the nitrocarburising atmosphere depend on the reverse water-gas reaction :



The production of carbon monoxide by means of reaction (3) is of particular importance in obtaining an atmosphere of sufficiently high carbon activity when carbon dioxide is used as a carbon bearing feedstock. If the atmosphere is composed of an ammonia and endogas mixture with an inherent high content of carbon monoxide then the carbon activity will be high and from the work of Grabke<sup>10,11)</sup> it is known that the dominant carburising reaction at 570°C, a typical ferritic nitrocarburising temperature, is :



$$a_c = K_3 \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

The presence of carbon during nitrocarburising stabilises the epsilon phase so that it will form much lower nitrogen activities than in the absence of carbon. It can be seen from Table 1 that the carbon activity for an endogas-ammonia mixture is

**TABLE 1.** Calculated quasiequilibrium compositions of various nitrocarburising atmospheres at 580°C : after Ref. 32

Added gas mixture	Quasiequilibrium Composition, vol %							Activities*		
	N <sub>2</sub>	H <sub>2</sub>	CO	H <sub>2</sub> O	CO <sub>2</sub>	NH <sub>3</sub>	HCN	a <sub>N</sub>	a <sub>C</sub>	a <sub>O</sub>
50% endogas	24.1	25.9	9.0	0.76	0.68	38.4	1.16	1620	22.4	0.072
50% NH <sub>3</sub>										
40% endogas	29.2	24.3	6.7	2.46	1.77	35.4	0.244	1650	4.81	0.25
10% air										
50% NH <sub>3</sub>										
5% CO <sub>2</sub>	58.8	15.5	2.9	2.98	1.45	18.4	0.045	1680	1.09	0.48
60% N <sub>2</sub>										
35% NH <sub>3</sub>										
5% CO <sub>2</sub>	54.4	15.9	6.4	2.22	2.31	18.6	0.135	1640	3.32	0.34
5% CO										
55% N <sub>2</sub>										
35% NH <sub>3</sub>										
5% CO <sub>2</sub>	45.4	26.6	3.4	3.50	1.16	19.9	0.049	806	1.88	0.33
20% H <sub>2</sub>										
45% N <sub>2</sub>										
30% NH <sub>3</sub>										

\*The reference states for the activity values are nitrogen gas at 1 atm, graphite, and wustite for nitrogen, carbon, and oxygen respectively.

markedly higher compared to that of nitrogen based atmospheres. However, the carbon activity of endogas based atmospheres can be reduced, if required, by means of, for example, addition of air, while for nitrogen based atmosphere the carbon activity can be increased by addition of, for example, carbon monoxide.

The carbon activity and oxygen activity are related to each other when equilibrium conditions prevail. The effect of oxygen or combined oxygen additions to a nitrocarburising atmosphere is to lower the carbon activity in the gas phase. Hence the presence of oxygen is now recognised as an important constituent in the atmosphere if good quality nitrocarburising is to result, i.e., with a monophased  $\epsilon$  structure. The importance of this has been emphasised by Slycke and Sproge through their studies of the hydrogen cyanide carbon mass transfer Reaction(2). In this reaction it can be seen that for each nitrogen atom transferred by Reaction (2) one carbon atom is also transferred. This leads to a build up of carbon in the compound layer, and eventually the formation of cementite(which is undesirable) unless carbon is taken care of by the decarburising Reaction(4) with a sufficiently low carbon activity, which can be brought about by the presence of oxygen in the atmosphere.

### COMPOUND LAYER FORMATION

Traditionally, it has been accepted that the range of solubilities of carbon and nitrogen for a stable  $\epsilon$ -carbonitride phase can be derived from the isothermal section of the Fe-C-N phase published by Nauman and Langerscheid in 1965<sup>12)</sup>. However, in 1983 Wells and Bell<sup>13)</sup> clearly demonstrated that stable  $\epsilon$  phases can be produced with lower interstitial contents than those predicted by the ternary phase diagram and their data are included in Fig.2. It is not known whether or not the presence of oxygen within the  $\epsilon$  phase influences the phase limits or not, but recently Xu and Li<sup>14)</sup> have expressed the opinion that a reduction in the partial pressure of oxygen would considerably change the structure of the phase field. However, it is clear that the structure of the compound layer

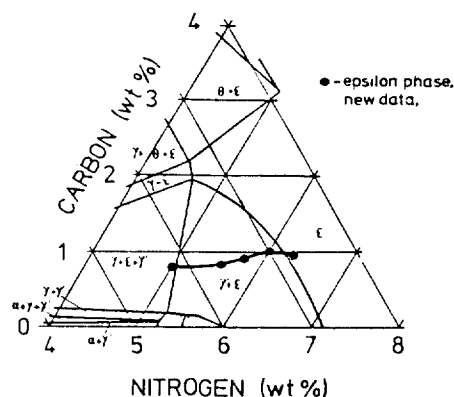


Fig. 2. Auger electron spectroscopy carbon and nitrogen concentration data for epsilon mono phased compound layer produced using methanol/ammonia mixtures superimposed on the iron-carbon nitrogen ternary phase diagram according to Naumann and Langerscheid<sup>12)</sup>. The five datum points of the epsilon phase derived by Wells and Bell<sup>13)</sup> are clearly in disagreement with the epsilon phase limits depicted by the ternary diagram.

resulting from a nitrocarburising treatment cannot necessarily be predicted or explained by reference to the Nauman and Langerscheid version of the iron-carbon-nitrogen system. Accordingly, there has been considerable interest in recent years in a reappraisal of the Fe-C-N system. In 1987 Xu and Li<sup>14)</sup>, by thermodynamic calculation showed that the Fe<sub>4</sub>N region of the Nauman and Langerscheid Fe-C-N ternary phase diagram was correct, but that the  $\epsilon$  region required revision. Furthermore, their calculations showed that most of the experimental data given by Wells and Bell were reasonable. Further experimental data, which has been reviewed by Slycke et al<sup>15)</sup>, and which is at variance with the Nauman and Langerscheid diagram includes the existence of a  $\epsilon$  + cementite two-phase field around 570°C by Mittemeijer et al<sup>16)</sup>, Colijn et al<sup>17)</sup>, Mittemeijer<sup>18)</sup> and Wells and Bell<sup>13)</sup>. In addition, during nitriding it has been observed that the pearlitic cementite in low alloy steels transforms to  $\epsilon$ <sup>16,17,18)</sup>. Thus, at the transformation front,  $\alpha$ ,  $\epsilon$  and cementite can be in contact with each other, indicating the existence of an  $\alpha + \epsilon + \text{Fe}_3\text{C}$  three

-phase field. On the basis of such new experimental data Slycke et al.<sup>19</sup> have proposed a new ternary phase diagram for the iron Fe-N-C system at

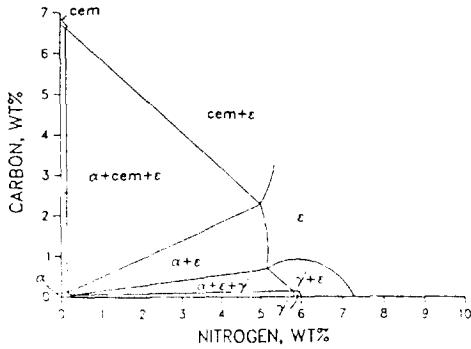
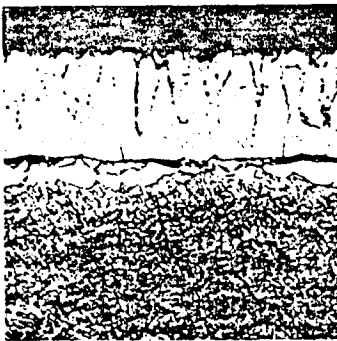


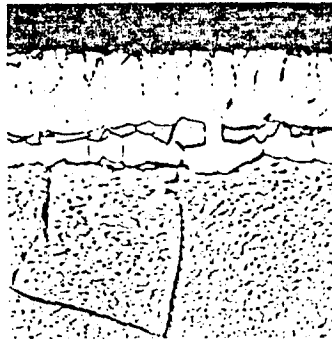
Fig. 3. Tentative Fe-N-C phase diagram at 570-580°C. Sizes of  $\alpha$ ,  $\gamma'$  and cementite fields are not in scale<sup>(15)</sup>.

temperatures around 570°C. This new diagram, which is shown in Fig. 3, allows for the direct contact between the ferrite and  $\epsilon$  phase which, as described above, is frequently observed during nitrocarburising. Use of this diagram has been shown by Slycke and Sproge<sup>8)</sup> to eliminate all ambiguity regarding the interpretation of how the compound layer structure is evolved under a wide variety of steel processing conditions.

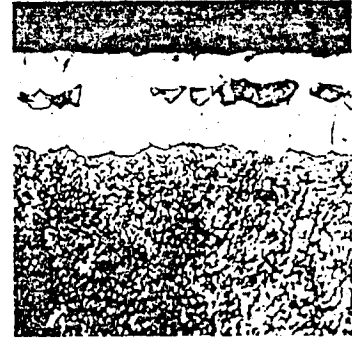
By way of example of the use of the new Fe-C-N phase diagram consider the series of micrographs in Fig. 4 from the work of Wells and Bell<sup>19)</sup> after nitrocarburising pure iron (99.9%) in various methanol ammonia mixtures. The structure typical of compound layers formed at low methanol/ammonia ratios is illustrated in Fig. 4 a. X-ray structural analysis demonstrated that the layer is composed predominantly of the epsilon iron-carbon-



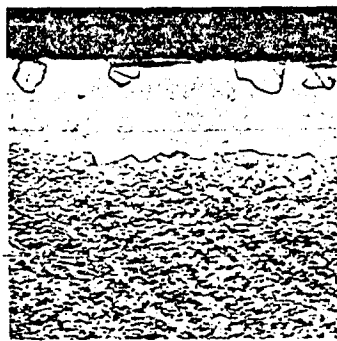
(a) 20% methanol/80% ammonia



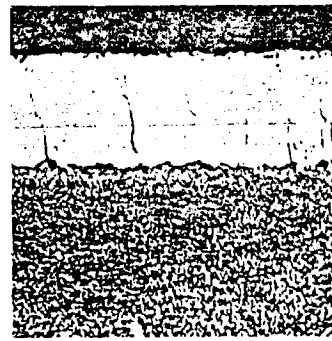
(b) 30% methanol/70% ammonia



(c) 40% methanol/60% ammonia



(d) 43% methanol/57% ammonia



(e) 50% methanol/50% ammonia



(f) 70% methanol/30% ammonia

Fig. 4. Compound layers formed on iron by gaseous nitrocarburising in various ratios of methanol/ammonia. Quenched samples, all X 100 (a, c, d, e, f etched in alcoholic ferric chloride and hydrochloric acid with iodine; b etched in Nital with ferric chloride)<sup>19)</sup>.

ide phase. The darker band structure seen in the layer was found to consist of the  $\gamma'$  iron nitride phase which has very restricted carbon solubility. As the methanol/ammonia ratio in the treatment atmosphere increased, the position of the  $\gamma$  phase band structure in the compound layer was increasingly displaced away from the layer/matrix interface, as can be seen in Figs. 4b-d. At an atmosphere composition of 45-60% methanol/55-40% ammonia a layer was formed which is free of the  $\gamma$  phase, or any other detectable secondary phase, and may be described as an epsilon carbonitride monophased layer (Fig.4e). The compound layers which were formed in atmosphere with a methanol content in excess of 60% are typified by the structure shown in Fig.4f. The layer is thin, duplex in character and contains a phase which was identified by X-ray structural analysis as cementite. Schematic representations of the surface compositions from each sample in the series and the resulting gradients from their trails are superimposed in the new Fe-C-N phase diagram in Fig.5, where it can be seen that there is good agreement with the corresponding phase analysis description outlined above.

Similarly, Slycke and Sproge<sup>8)</sup>, have demonstrated that if a high carbon steel is treated in atmospheres over a wide range of carbon activities the following sequence of events may occur.

- Ferrite and cementite dissolve nitrogen
- Cementite transforms into epsilon phase via Ferrite + Cementite  $\rightarrow$  Ferrite + Epsilon
- Epsilon phase grows at the expense of ferrite until a covering compound layer is formed
- Continued growth of the monophased compound layer is controlled by nitrogen diffusion

A schematic representation of compound layer formation on a high carbon steel is shown in Fig.6, and a corresponding micrograph in Fig.7<sup>9)</sup>.

It is clear from the foregoing review that over the past fifteen years the physical metallurgy basis for gaseous ferritic nitrocarburising has been strengthened considerably. It can now provide the scientific underpinning essential for the continued

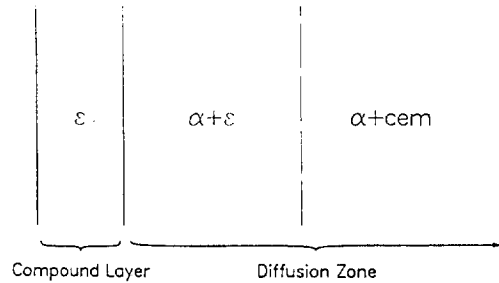


Fig.6. Schematic sequence of phase development during nitrocarburising of high carbon steel<sup>9)</sup>.

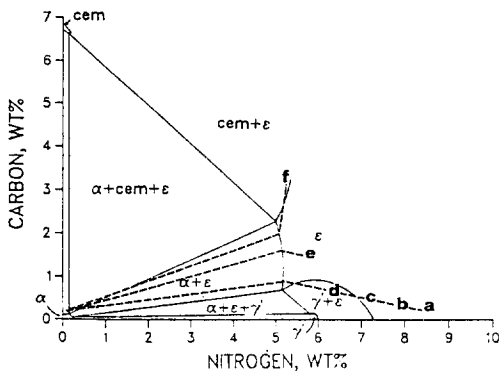


Fig.5. Schematic representation of the surface composition of the micrographs in Fig.4 a-f, superimposed on the new schematic ternary Fe-N-C phase diagram.

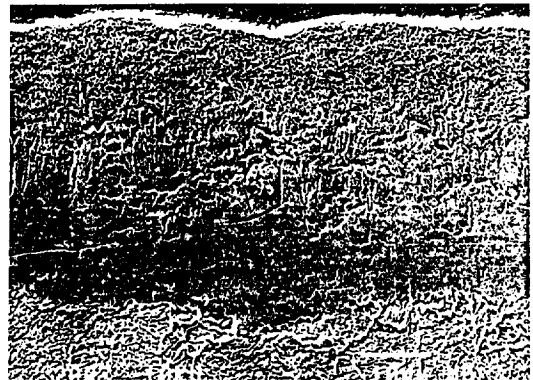


Fig.7. Compound layer structure of high carbon steel nitrocarburised in  $N_2 + 35\% NH_3 + 5\% CO_2$  atmosphere at 580°C, for 2 hrs. SEM backscatter mode. Corresponds to schematic in Fig.6.

rapid acceptance of nitrocarburising by manufacturing industry, which was largely not available when Bell<sup>6)</sup>, in 1975, on the basis of all the information available concerning salt bath treatments concluded that for a compound layer to exhibit good tribological properties it should consist essentially of the  $\epsilon$  carbonitride phase. Furthermore, this was considered to be a prerequisite for any commercially successful gaseous nitrocarburising process.

### DIFFUSION ZONE CHARACTERISTICS AND FATIGUE PROPERTIES

The diffusion zone characteristics are essentially independent of the type of nitrocarburising media used<sup>9)</sup>. During the treatment of plain carbon steels with a large proportion of ferrite, only nitrogen diffuses in from the carbonitride compound layer, since the ferrite is normally already at its equilibrium concentration with respect to carbon. However, some outward carbon diffusion from high carbon concentration regions of the matrix into the compound layer can be experienced with most grades of steel and cast iron<sup>2)</sup>. Whilst contributing to the quality of the compound layer this loss of carbon is thought to have no effect on the fatigue resulting from the diffusion zone. The diffusion zone beneath the compound layer for oil quenched samples is indistinguishable from the original matrix material on an optical metallographic basis (Fig.1), however fine scale precipitation of nitrides can be observed by TEM following oil quenching<sup>19)</sup>. Nevertheless by rapid cooling it is possible to retain most of the nitrogen in supersaturated solid solution and in this condition it increases both the yield strength of the base material and its fatigue strength. Indeed, both the bending fatigue strength<sup>19)</sup> and rotating bend fatigue strength<sup>7)</sup> of low carbon steels can be increased by more than 120%, Fig.8. However, ageing, like atmosphere cooling from the treatment temperature, substantially decreases the fatigue strength<sup>19)</sup>. The improvement in fatigue properties is directly related to the depth of nitrogen diffusion as can be seen in Fig.9 from the work of Dawes and Tranter<sup>20)</sup>. By using a sufficiently long nitrocarburising time it is possible

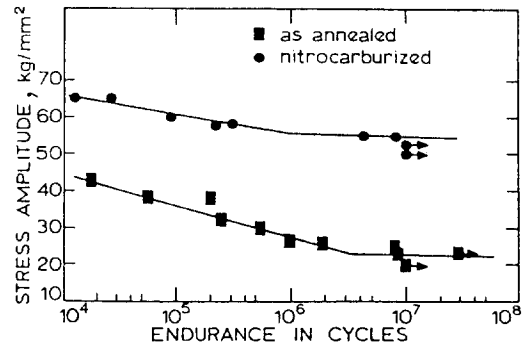


Fig.8. Wohler fatigue curves for unnotched specimens of untreated and gaseous nitrocarburised mild steel<sup>2)</sup>.

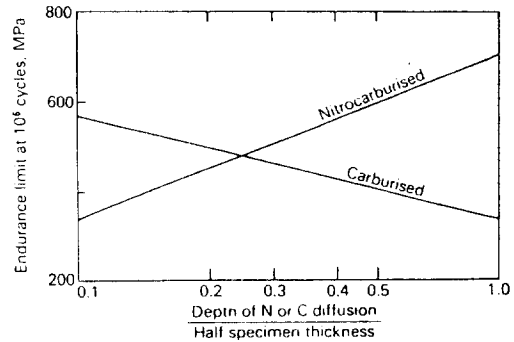


Fig.9. Fatigue strength of low-carbon non-alloy steel nitrocarburised at 570°C or carburised at 900°C<sup>20)</sup>.

to achieve this fatigue improvement throughout the component section. This is in contrast to conventional surface hardening processes such as carburising and carbonitriding of non-alloy steels and the nitriding of alloy steels, where a fatigue strength improvement is obtained as a result of a combination of surface strengthening and by the introduction of a surface compressive macro-stress. It has been suggested by Mittemeijer<sup>21)</sup> that for nitrocarburised plain carbon steel the residual microstresses can have a decisive influence on the endurance limit, even for notched components, since clearly for through hardened nitrocarburised materials there must be zero macro-residual stress effects.

## INDUSTRIAL GASEOUS AUSTENITIC NITROCARBURISING

In 1961, before the availability of this detailed structural and chemical analysis of the compound layer on salt bath nitrocarburised materials, a patent had been applied for by Joseph Lucas (Industries) Ltd. for a type of gaseous nitrocarburising<sup>22)</sup>. This treatment produced, on mild steel, a porous layer which was claimed to have good anti-frictional properties. The complete patent, when published, revealed that the gaseous atmosphere consisted of ammonia and hydrocarbon or other carbon containing gases of unspecified proportions and that the treatment was undertaken in the temperature range 450–590°C. At that time, however, no detailed technical specification of the property improvements achieved, or of the structures which were responsible, was published. During the 1960's further research led to consideration of a large range of gaseous nitrocarburising processes throughout the world. A wide variety of atmospheres were proposed and, indeed, employed in these processes. These included triethanolamine<sup>23)</sup>, ammonia/kerosene<sup>24)</sup> and isopropanolwater/urea/ammonia<sup>25)</sup>. However, it was only in the early 1970's that gaseous nitrocarburising received serious industrial attention with the introduction of a variety of gaseous techniques.

### Nitemper<sup>(R)</sup> Process<sup>26)</sup>

This process is usually carried out in Ipsen sealed quench furnaces and uses an inert atmosphere consisting of 50% ammonia and 50% endothermic gas. The treatment temperature is 570°C and treatment times usually between 1 hour and 3 hours are used, after which the components are either quenched into oil or cooled under recirculated protective gas<sup>26)</sup>. By 1975 the Nitemper process had been in use for several years and furnaces performing the treatment were in operation in Germany, Sweden, USA, Japan and the United Kingdom for improving the scuffing and fatigue resistance of ferrous engineering components. The treatment is now used extensively throughout the

world and the possibility of a two-stage Nitemper process is being developed<sup>27)</sup>. This involves the use of an atmosphere with a high carbon dioxide level in the initial stage to promote rapid compound layer formation. The influence of controlled additions of CO<sub>2</sub> to ammonia based nitrocarburising atmospheres under industrial conditions has recently been investigated by Vogel for a wide range of alloy steels. He demonstrated quite clearly that the proportion of the  $\epsilon$  phase in the compound layer increased with increasing carbon dioxide content, i.e. lower carbon activities and that the  $\epsilon$  phase more readily formed on alloy steels than on pure iron, or plain carbon steels (Fig.10). These observations are in keeping with the detailed mechanisms of carbon availability from the substrate discussed by Slycke and Sproge<sup>8)</sup>. In the second stage of the modified Nitemper process an atmosphere with a high carbon monoxide content is employed to increase the carbon content of the compound layer for enhanced wear resistance. In essence, therefore, the process involves a combination of the Nitroc Process<sup>29)</sup>, which utilises unpurified exothermic gas as the carburising medium, and the traditional Nitemper technology. A similar duplex treatment called Deganit has been proposed by Eysell<sup>30)</sup>.

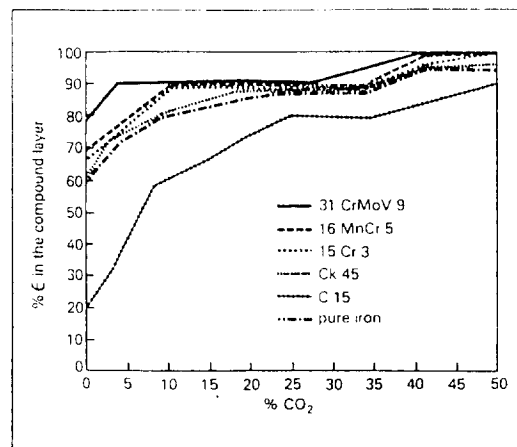


Fig.10. The influence of CO<sub>2</sub> addition to ammonia on the structure of the compound layer, formed by nitrocarburising at 580°C, on pure iron, plain carbon steels and low alloy steels<sup>28)</sup>.



Alnat-N Process<sup>31)</sup> A recent publication by McGeever et al<sup>32)</sup> describes a patented approach to nitrocarburising whereby nitrous oxide is incorporated in the atmosphere to enhance, through the indirect presence of oxygen, the rate of formation of the compound layer, thus endorsing a feature clearly demonstrated by Dawes et al in 1973<sup>33)</sup>. A further feature of the Alnat-N process is that the addition of a carburising gas to the basic  $\text{NH}_3/\text{N}_2\text{O}/\text{N}_2$  mixture is claimed to be unnecessary. Thus the incorporation of carbon into the compound layer must be via diffusion from the matrix materials. Control of Gaseous Nitrocarburising Atmospheres

#### Control of Gaseous Nitrocarburising Atmospheres

A possible limitation on the gaseous nitrocarburising processes developed in the mid-1970's was that optimum processing conditions for all classes of material, including cast irons, tool and stainless steels could not be assured. A further and perhaps more serious limitation was that reproducibility could be impaired with variable loads and from furnace to furnace. These difficulties were in part overcome through the use of infra-red monitoring and control systems<sup>9)</sup>. However, gas analysis of atmospheres containing both ammonia and carbon dioxide can be problematic, especially when high ammonia contents and high dew points are concerned. If water is condensed in the sample gas piping, high amounts of ammonia will dissolve and the resulting strong solution can dissolve large amounts of carbon dioxide. If this solution becomes super-saturated a mixture of ammonium carbonate and bicarbonate will precipitate out in the form of a white powder<sup>6)</sup>. Experience has shown that when such precipitation has occurred further measurement of ammonia and carbon dioxide is in error and there is a distinct likelihood that the pipeline of the measurement system will be blocked. Slycke and Sprøge<sup>8)</sup> have shown that this problem can be largely overcome by suitable heating of the measurement instrumentation and the gas sampling pipeline.

Because of limitations of the infra-red gas analysis approach to the control of gaseous nitrocarburising atmospheres attention has been

focussed recently on the development of solid electrolyte gas sensors for the measurement and control of the nitrogen and oxygen potentials of nitriding and nitrocarburising atmospheres<sup>34)</sup>. Such instruments are, in principle, similar to those widely used for carbon potential control of carburising gas atmospheres.

#### Black Nitrocarburising

Post nitrocarburising oxidation treatments have been used on a commercial basis since 1976 to enhance the aesthetic properties of gaseous nitrocarburised components for the hydraulics industry<sup>35)</sup>. However, in 1982 Dawes and Tranter<sup>20)</sup> showed how such black nitrocarburising treatments, including the Nitrotec process, could be used for the combined enhanced fatigue, wear and corrosion resistance of mild steel types of materials. They showed that this could be achieved by specifically designing a range of cost effective, aesthetically pleasing black oxidised electrical components for use in automobile manufacture.

Particular success has been achieved with ultra-low carbon vacuum degassed and niobium/titanium stabilised deep-drawing steels which have enabled many complex thin-sectioned components to be manufactured by single stage press operations. These steels have very low yield strengths of about 155 MPa with elongation values of approximately 45%. To achieve optimum engineering properties in the final component nitrocarburising can be used. The influence of quenching temperature on the yield strength of these nitrocarburised special steels is shown in Fig.11<sup>20)</sup>. It is clear that low temperature quenching has resulted in nitride precipitation and loss of strength, and that if a high strength is to be achieved a quenching temperature not less than 550° is necessary. As discussed earlier in the treatment of mild steel, this is also the condition for optimum enhancement of the fatigue strength. Another essential feature of this treatment is that distortion of thin sectioned material can be kept to a minimum by controlled quenching into an oil/water emulsion at a temperature of 70-80°C and that the quench time involved is sufficient to produce an aesthetically pleasing black oxide film of  $\text{Fe}_3\text{O}_4$ .

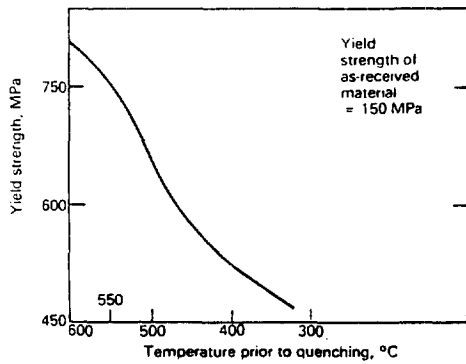


Fig.11. The influence of quenching temperature on the yield strength of nitrocarburised deep drawing steels<sup>20</sup>.

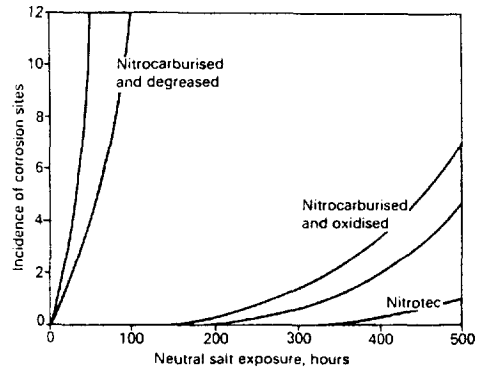


Fig.13. Relationship between treatment sequence and salt corrosion resistance (ASTM B 117)<sup>36</sup>.

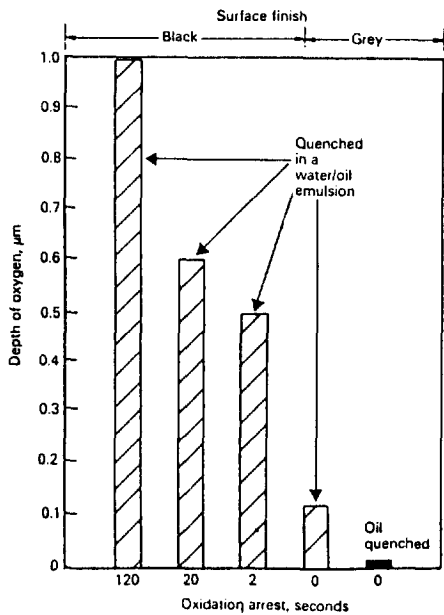


Fig.12. Influence of depth of oxygen on surface coloration and corresponding oxidation arrest time for various quench media<sup>20</sup>.

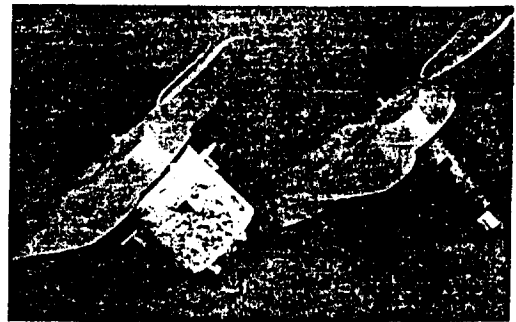


Fig.14. Electric fan motor treated by Nitrotec process and neutral salt spray tested for 250 hrs relative to zinc plated component<sup>20</sup>.

which needs to be less than 1.0 µm in thickness if exfoliation is to be avoided, Fig.12.

The flash oxidation parameters of the basic Nitrotec process are designed to produce an oxide structure capable of both conferring a degree of corrosion resistance and acting as a carrier for an organic sealant. Investigations into the composition of organic sealants has resulted in the development

of specific formulations which are based on either hydrocarbon-solvent-borne mixtures of metal soaps produced from rosin acids and oxidised petrolatums, or water based mixtures of emulsified microcrystalline and synthetic hydrocarbon waxes with corrosion inhibitors<sup>36</sup>.

The relative contributions of post-nitrocarburising oxidation and organic sealing to the overall corrosion resistance of the Nitrotec process is shown in Fig.13<sup>36</sup>. It can be seen that the degreased nitrocarburised surface itself imparts little inherent corrosion resistance. An example of an automotive fan motor treated by the Nitrotec process and tested relative to zinc plating is illustrated in Fig.14<sup>20</sup>. Other components now in service using the Nitrotec black nitrocarburising

process include windscreen wiper linkage assemblies which have been fitted since 1985 to Austin Rover's Metro, Maestro and Montego models<sup>37)</sup>. The Austin Rover 800 series also uses Nitrotec treated bumper armatures, while the Renault 25 series has the seat sliders treated. A particularly interesting 'high tech' application of the process is in the cost effective manufacture of the viscous slip differential used on Ford Sierra and BMW cars<sup>38)</sup>.

An alternative black nitrocarburising finish is Ashland Nitro Black, which is a patented process utilising fluidised bed technology<sup>39)</sup>. The atmosphere used for the nitrocarburising stage comprises a mixture of ammonia, natural gas and nitrogen. After nitrocarburising, the fluidised bed is purged with nitrogen for two minutes prior to the oxidation step during which steam and air are injected, via an integral coil system, to impart a thin  $Fe_2O_3$  layer on treated components. Fluidised bed quenching is then followed by coating with a proprietary polymeric emulsion sealant.

### AUSTENITIC NITROCARBURISING<sup>40)</sup>

Nitrocarburising has been defined by the Terminology Committee of the International Federation for Heat Treatment and Surface Engineering<sup>41)</sup> as a thermochemical treatment which is applied to a ferrous object in order to produce surface enrichment in nitrogen and carbon which forms a compound layer. Beneath the compound layer there is a diffusion zone enriched in nitrogen". When the treatment temperature is such that partial transformation of the matrix to austenite occurs, through enrichment with nitrogen, then the treatment is referred to as austenitic nitrocarburising.

Austenitic nitrocarburising was first developed as a cyanide salt bath process, under the trade name Noskuff<sup>42)</sup> and later an equivalent gaseous treatment was patented by Bell in 1977<sup>43)</sup>. The primary objective of the austenitic treatment is to overcome the principal disadvantage of ferritic nitrocarburising, namely, that with plain-carbon steel components there is no significant hardened case below the compound layer and, accordingly, the ability of components to withstand high Hertzian

stresses is restricted. Austenitic nitrocarburising, by which the sub-surface (but not the complete cross-section) is transformed to iron-carbon-nitrogen austenite, which is subsequently transformed to tempered martensite and bainite, with a hardness in the range 750-900 HV, provides a means of extending the range of applications of nitrocarburising treatments.

### PHYSICAL METALLURGY ASPECTS OF GASEOUS AUSTENITIC NITROCARBURISING

On the basis of extensive physical metallurgy studies at the Wolfson Institute for Surface Engineering, together with work by the Swedish Institute for Metal Research<sup>44,45)</sup>, it has been shown that gaseous austenitic nitrocarburising treatments can be carried out successfully in sealed quench furnaces using mixtures of endothermic and ammonia gases. Additional detailed laboratory studies have been conducted by Firrao et al<sup>46)</sup> into the growth kinetics and characterisation of compound layers formed on carbon steels by the action of methyl-alcohol saturated ammonia.

As with the ferritic nitrocarburising treatment, the compound layer should consist mainly of the c.p.h. epsilon carbonitride phase, which is predominantly responsible for significant improvements in tribological properties. Experimentally, this can be achieved quite readily in the temperature range 675-775°C and the 700°C isothermal section of the Fe-C-N phase diagram shown in Fig.15, after Naumann and Langenschei<sup>47)</sup>, seems quite adequate in describing the phase structures produced at this temperature.

By way of illustration of the structure and properties resulting from austenitic nitrocarburising, consider EN 32 steel (08 0 M 15) subjected to an austenitic nitrocarburising treatment at 700°C with a 15% residual ammonia level in the exhaust gas atmosphere of a sealed-quench furnace. The appropriate microstructure after 1 hour treatment is shown in Fig.16<sup>40)</sup> X-ray diffraction analysis has revealed that the 50  $\mu$ m thick compound layer consists predominantly of the epsilon phase. The

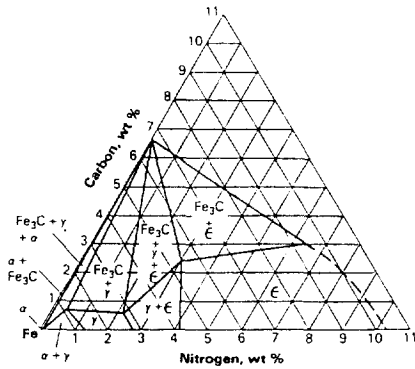


Fig. 15. Isothermal section of the Fe-C-N phase diagram at 700°C (after Naumann and Langerscheid<sup>12)</sup>).

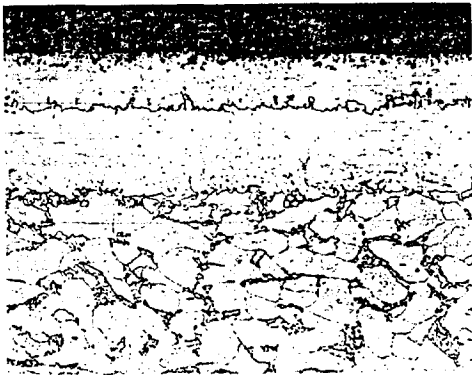


Fig. 16. Micrograph of EN 32 nitrocarburised for 1 hr at 700°C in ammonia/endothermic gas with 15% residual ammonia and oil quenched<sup>40)</sup>

corresponding interstitial profile analysis, as performed with a calibrated electron probe/microanalyser<sup>47)</sup> are shown in Fig. 17. It can be seen by reference to Fig. 17 that at least the outermost portion of the compound layer falls within the desired monophased epsilon carbonitride region. The kinetics of growth of the compound layer obey a parabolic law, as shown in Fig. 18, thus illustrating the diffusion-controlled nature of compound layer formation. The hardness profile of the as-quenched nitrocarburised layer is plotted in Fig. 19. It can be seen clearly that there is a dip in the hardness value at the compound layer/austenite interface

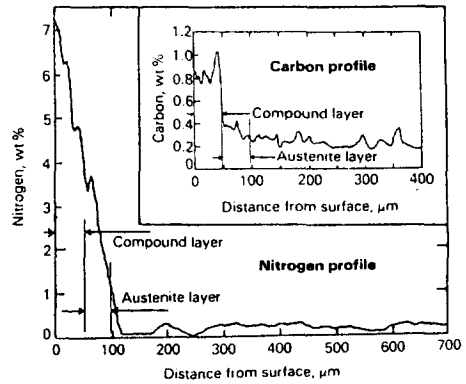


Fig. 17. Carbon and nitrogen profiles for EN 32 nitrocarburised for 1 hr at 700°C in ammonia/endothermic gas with 15% residual  $\text{NH}_3$ <sup>40)</sup>.

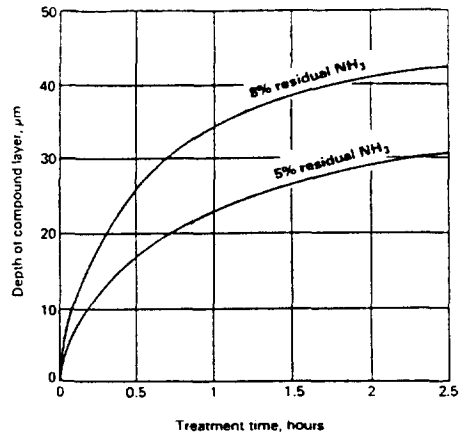
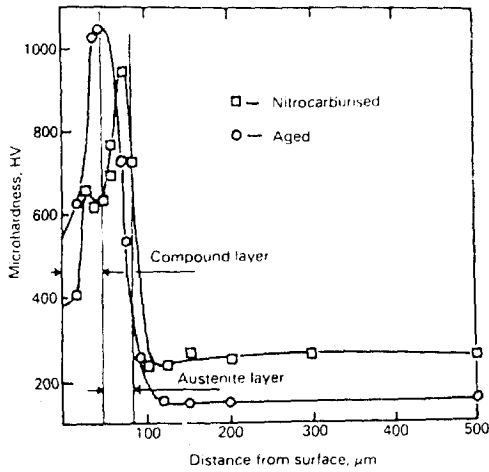


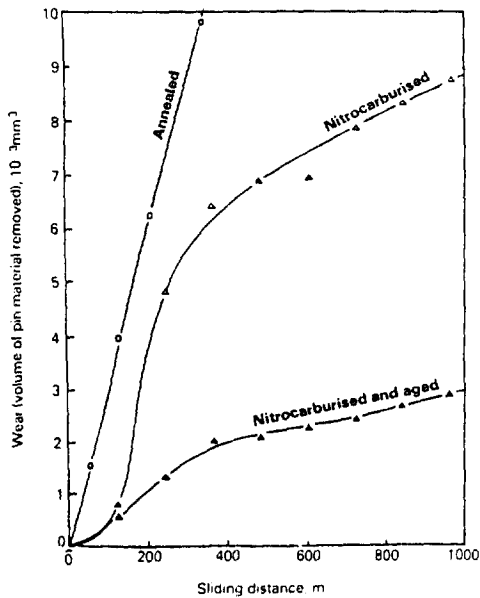
Fig. 18. Growth kinetics of the compound layer at 700°C in ammonia/endothermic gas with different residual ammonia levels<sup>40)</sup>.

associated with the high contents of nitrogen and carbon in solution which depresses the  $M_s$  temperature to below ambient. As a result of ageing this hardness dip is removed due to the fine-scale formation of iron-nitrogen bainite.

As with ferritic nitrocarburising the presence of the compound layer significantly enhances the wear resistance, as is illustrated in Fig. 20. Similarly, there is a major enhancement in the fatigue strength (circa 100%) both directly after quenching, and after quenching and ageing<sup>40)</sup>.



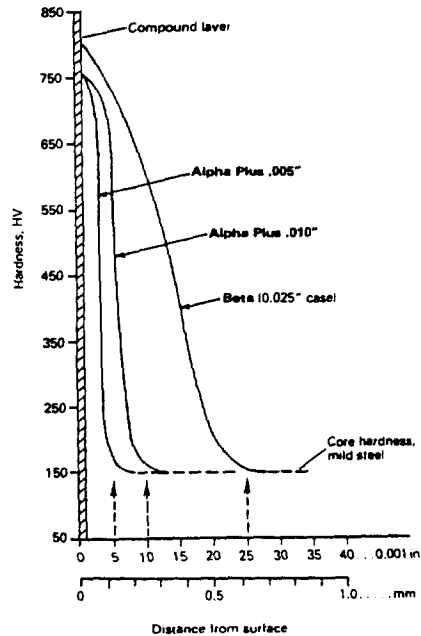
**Fig.19.** Microhardness profiles for austenitic nitrocarburised mild steel before and after ageing at 250°C for 2 hrs. Nitrocarburised for 1 hr at 700°C in ammonia/endermoric gas with 15% residual NH<sub>3</sub> and oil quenched<sup>40</sup>.



**Fig.20.** Wear rates of mild steel in the annealed, austenitic nitrocarburised and aged conditions. Nitrocarburising at 700°C for 1 hr in ammonia/endermoric gas with 15% residual ammonia, oil quench. Aged at 250°C for 2 hrs. Pin-on-disc test involving treated mild steel pin and carbonitrided EN 8 disc.

### INDUSTRIAL GASEOUS FERRITIC NITROCARBURISING

It has been illustrated above that in order to obtain maximum sub-surface strength, it is necessary to transform the austenitic zone beneath the compound layer into iron-nitrogen (carbon)bainite. Typical transformed austenite case thicknesses are in the range 50-200 µm, with a hardness of between 750-900 HV. However, much deeper cases can be achieved by employing a pre-carburising treatment prior to nitrocarburising<sup>43</sup>. These variants of the austenitic nitrocarburising process have been exploited commercially with the Alpha Plus and Beta industrial processes<sup>18</sup>. Typical hardness profiles resulting from these treatments, using a carrier gas of nitrogen/methanol enriched with ammonia and natural gas, are illustrated in Fig. 21<sup>48</sup> and typical Industrial applications are summarised in



**Fig.21.** Hardness profiles resulting from three austenitic nitrocarburising treatments applied mild steel<sup>48</sup>.

TABLE 2. Production applications of austenitic nitrocarburising

Austenitic nitrocarburising treatment type	Applications
Alpha Plus. 005" (0.125mm underlying case)	Clutch plates, levers, gears, bushes, thin pressings
Alpha Plus. 010" (0.25mm underlying case)	Gears, levers, pulleys, liners, etc.
Beta (0.60mm underlying case)	Machine slideways, guide bars, gears, sprockets, pins, bushes, waterpump parts, liners, jigs/fixtures, bearings, etc.

Table 2. An indication of the major benefits to be exploited through such treatments are illustrated with a variety of components in Fig. 22. Recently, a 'deep case' variant of the Nitrotec process has been introduced, known as Nitrotec C<sup>(49)</sup>. In essence, this is a 'black' austenitic nitrocarburising process, whereby a precarbured substrate is subsequently processed to produce the surface  $\epsilon$  compound layer at a temperature which allows for hardening of the carburised zone during quenching.

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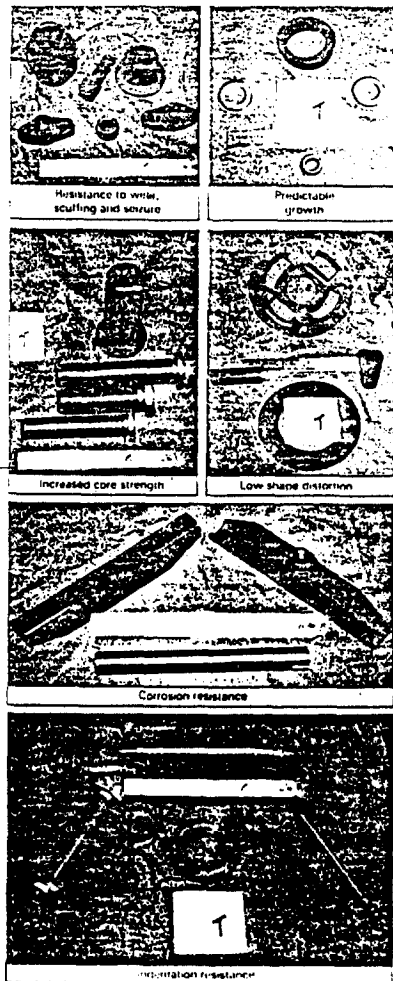


Fig. 22. Typical examples of austenitic nitrocarburised components, with an indication of the major benefits exploited<sup>(48)</sup>.

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