Abstract
Plasma carbonitriding, even though being a relatively new procedure among complex heat treatments, has managed to attract more and more interest towards it. So it was possible to determine the scientific fundaments of the physical-chemical and metallurgical phenomena which unfold during this treatment. The process is especially suitable for complex parts that are intensively solicited by wear, fatigue, contact pressure, shocks, possibly also to corrosion. It is applied in order to bring the metallic products in a state favourable from the point of view of structure, chemical composition and internal stress state. This state corresponds to a precise association of properties (according to the processing technologies and their stressing during functioning).

The paper presents an analysis of the structures and characteristics of a widely used structural steel (39MoAlCr15, containing 0.35…0.42%C; 0.35…0.60%Mn; max. 0.035%S; max. 0.035%P; 1.35…1.65%Cr; 0.15…0.25%Mo; 0.20…0.45%Si; 0.70…1.10%Al) subjected to the plasma carbonitriding process.

1. INTRODUCTION
Carbonitriding has been defined as a thermochemical treatment which is applied to a ferrous object in order to produce surface enrichment in nitrogen and carbon, which form a compound layer. Beneath the compound layer there is a diffusion zone enriched in nitrogen [1]. When the treatment is carried out at a temperature below the eutectoid temperature, i.e., when the material of the diffusion zone is in the ferritic state, the treatment is the well-established ferritic carbonitriding process [2] for the enhancement of scuffing, fatigue and corrosion properties of ferrous materials. When the treatment temperature is such that partial transformation of the matrix to austenite occurs through enrichment with nitrogen, the treatment is referred to as austenitic carbonitriding.

The primary objective of the austenitic carbonitriding treatment ([3], [4]) is to overcome the main disadvantage of ferritic carbonitriding, namely that with carbon steel components there is no significant hardened case beneath the compound layer and accordingly the ability of components to withstand high hertzian stresses is restricted. Austenitic carbonitriding, 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 of 750-900 HV, provides a means of extending the range of applications of carbonitriding treatments.

Based on extensive physical metallurgy studies found in the speciality literature ([5], [6]), it has been shown that gaseous austenitic carbonitriding treatments can be carried out successfully in sealed quench furnaces using as processing atmospheres mixtures of endothermic and ammonia gases, with the nitriding potential controlled by means of infrared gas analysis.
The goal of this paper is to summarise the current status of austenitic carbonitriding and to illustrate the metallurgical principles involved, using, where possible, a single material - the steel 39MoAlCr15 (0.35...0.42% C; 0.35...0.60% Mn; 1.35...1.65% Cr; 0.15...0.25% Mo; 0.20...0.45% Si; 0.70...1.10% Al; max. 0.035% S; max. 0.035% P) and a single processing temperature (700°C).

2. CURRENT STATUS OF AUSTENITIC CARBONITRIDING

Optimum treatment temperatures are in the range 675-775°C; at higher temperatures, thermal dissociation of ammonia is so great, that successful carbonitriding is not possible. Processing times in excess of 1-2 hours do not appear to be justified. Optimum atmosphere conditions involve inlet gas mixtures containing between 65-70% NH₃ and 30-35% endothermic gas, with the gas flow rates adjusted so as to exhibit a residual ammonia level of between 7-15% in the furnace.

The compound layer morphology is largely controlled by the processing temperature, but it is the level of non-dissociated ammonia that mainly dictates the compound layer thickness. Short treatment times generally result in a more compact and less porous compound layer and the optimum layer thickness is about 30µm.

As with the ferritic carbonitriding treatment, the compound layer consists mainly of the c.p.h. e carbonitride phase, which is predominantly responsible for significant improvements in the tribological properties. The average nitrogen content of good-quality compound layers is about 6-7 wt% and carbon levels are usually maintained at less than 1%. The microhardness of the compound layer is about 870 HV at the surface region and decreases to about 600 HV near the austenite boundary.

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. Optimum transformation hardening temperatures vary for different base materials, but typically lie in the range 250-300°C. Typical transformed austenite case thicknesses are in the range 50-200µm, with a hardness between 750-900 HV. However, much deeper cases can be achieved by employing a pre-carburising treatment prior to carbonitriding.

The fatigue strength of plain carbon steels is increased by between 60-100% after direct quenching from the austenitic carbonitriding temperature and is comparable with or slightly less than the improvement observed with ferritic carbonitriding. However, applying an ageing treatment on the sub-surface austenite area results in a small reduction in the level of enhancement of the fatigue strength, particularly at high stress cycles.

Industrial applications of austenitic carbonitriding are increasing rapidly using both plain-carbon and low-alloy case-hardening grades of steel. Typical applications for wear resistance include gears, drive shafts, pump parts, hand-brake ratchets and pulleys. Typical applications for enhanced fatigue life include crankshafts, steering pins, guide shafts and rocker arms. In addition, applications are being found where the minimal degree of distortion associated with the treatment is of benefit and, accordingly, components such as bevel gears, which were previously carbonitrided at 870-950°C, are now subjected to the austenitic carbonitriding treatment.

3. PRINCIPLES OF GASEOUS CARBONITRIDING

The basic requirement of all gaseous carbonitriding processes is to provide an atmosphere which allows nitrogen and carbon to be added simultaneously to the surface of ferrous materials and so produce the desired epsilon phase. For a processing temperature of 700°C for example, the relevant isothermal section of the Fe-C-N ternary system is shown in figure 1.
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[7], which illustrates the appropriate levels of nitrogen and carbon necessary to form the epsilon (e) carbonitride phase. The mass transfer of these levels of nitrogen and carbon involves mainly two reactions, occurring simultaneously: a nitriding reaction and a carburising reaction. Generally, ammonia gas is used for the nitriding reaction, while endothermic gas is frequently employed for usage in the carburising reaction. Obviously, the nitriding and the carburising reactions are interrelated with each other, depending on the processing temperature and the variations in both the carbon and nitrogen potentials of the atmosphere. Nevertheless, it is convenient if both reactions are dealt with separately.

In the carburising part of the reaction endothermic gas of the following nominal composition is involved: 35-40% N\textsubscript{2}; 15-25% CO; 0.3-0.4% CO\textsubscript{2}; 35-45% H\textsubscript{2}; 0.05-0.15% CH\textsubscript{4}; 0.2% H\textsubscript{2}O.

This gas contains methane and carbon monoxide, both of which can provide carbon, which diffuses into the surface in accordance with the following reactions:

\begin{align*}
\text{CH}_4 &\rightarrow \text{C}_\text{Fe} + 2\text{H}_2 \\
2\text{CO} &\rightarrow \text{C}_\text{Fe} + \text{CO}_2
\end{align*}

However, since the level of methane is so small within the endothermic gas, it can be assumed that the only effective carburising gas is carbon monoxide. Hence, the carburising potential of the furnace atmosphere is a function of the ratio \(p^2\text{CO}/p\text{CO}_2\), where \(p\text{CO}\) and \(p\text{CO}_2\) are partial pressures of CO and CO\textsubscript{2} respectively.

The endothermic gas composition can be readily adjusted to provide a high degree of flexibility over the control of the carburising potential through the CO\textsubscript{2} level. In industrial practice, however, the carbon potential is kept constant to provide a constant carbon level of less than 1% and only the nitrogen potential is adjusted to ensure that the epsilon carbonitride phase predominates on the surface of the component.

In the nitriding part of the reaction ammonia dissociates catalytically at the metal surface according to the reaction:

\[\text{NH}_3 \rightarrow \text{N}_\text{(Fe)} + \frac{3}{2}\text{H}_2\]

The nitrogen in the active condition diffuses into the metal surface being treated, while the atomic hydrogen forms hydrogen gas. Ammonia gas also thermally dissociates at the processing temperature to give nitrogen and hydrogen gases. However, since the solubility of nitrogen gas in the carbonitride phase and in austenite at one atmosphere pressure is extremely restricted [8], the nitrogen potential of the nitrogen gas can be regarded as being
negligible. Therefore, the level of dissociation and hence the nitriding potential at a given temperature is dictated by:

(i) the nature of the furnace materials;
(ii) the surface area and surface finish of the componenets;
(iii) the gas flow rate and turbulence characteristics of the furnace.

Due to the high level of free nitrogen gas within the furnace, it is not possible to determine the nitriding potential directly from the exhaust gas composition. However, a method has been formulated, [9], for evaluating the nitriding potential in ammonia-hydrogen mixtures using inlet volume fractions of ammonia and hydrogen together with the exhaust ammonia content. The same principles can be applied to determine the nitriding potential (\( r_N \)) in an ammonia/endothermic gas mixture from the following formula:

\[
r_N = \sqrt[4]{\frac{F}{\frac{1}{2} \frac{2 y (1 + F) + 3 (x - F)}{2 (1 + x)}}}
\]

where \( x \) is volume fraction of inlet ammonia, \( y \) is volume fraction of hydrogen in the endothermic gas and \( F \) is volume fraction of ammonia in the exhaust gas, as measured usually by infra-red gas analysis. In industrial practice, by keeping the endothermic gas composition constant, the exhaust ammonia is taken as a reasonable measure of the nitrogen potential, but for thermodynamic studies this is not reliable and the above formula should be employed.

4. STRUCTURES AND PROPERTIES RESULTING FROM AUSTENITIC CARBONITRIDING

Compound layer. As a practical example, a sample of 39MoAlCr15 steel subjected to an austenitic carbonitriding treatment at 700°C with a 15% residual ammonia level in the exhaust gas atmosphere of a sealed-quench furnace, will be analysed. It is known, [10], that these conditions provide a sufficiently high nitriding potential to produce the desired epsilon phase at the outermost surface and a sub-surface austenitic zone. The appropriate microstructure after a 1 hour treatment is shown in figure 2.

X-ray diffraction analysis has revealed that the 50 µm-thick compound layer did consist predominantly of the epsilon phase. The corresponding analyses of the interstitial profile, performed with the help of a calibrated electron probe/microanalyser, [11], are shown in figure 3.

It can be seen by reference to figure 1 that at least the outermost portion of the compound layer falls within the desired monophase epsilon carbonitride region. The kinetics of growth of the compound layer obey a parabolic law, as shown in figure 4, thus illustrating the diffusion-controlled nature of compound layer formation.

Decomposition of the austenite zone. The morphology and kinetics of the decomposition of hypereutectoid iron-nitrogen austenite to nitrogen bainite have been studied extensively ([12], [13], [14]). The net effect of this fine-scale bainite formation is shown on an optical micrographic scale in figure 6; as a result there is a very significant increase in the matrix hardness as is illustrated in figure 7.

Accordingly, when the nitrocarburised 39MoAlCr15 steel is aged at a suitable temperature, the zone beneath the epsilon compound layer undergoes the reaction described above, with a subsequent increase in hardness of the prior austenite region. This situation is illustrated in figure 5.
Wear and fatigue resistance enhancement. One of the benefits of the carbo-nitriding treatment is the significant improvement in wear resistance conferred by the presence of the compound layer. This is shown in figure 8, [10], in the form of results of a pin-on-disc wear test. It can also be seen that the hardening of the substrate, as a result of the presence of a bainitic/martensitic structure, significantly enhances the wear resistance.

A further important benefit, which arises from the nature of the diffusion zone, is the improvement in fatigue resistance conferred by carbo-nitriding (figure 9). It has been reported that the fatigue strength of a low-carbon steel is decreased somewhat after ageing, and this is in agreement with other observations [5], [6].
It is claimed that this reduction is associated with an embrittlement of the compound layer and a reduction in the compressive residual stress level within the compound layer. However, work on ferritic carbonitriding has frequently shown that the compound layer has virtually no effect on the fatigue properties. Indeed when the compound layer is removed the fatigue strength in a rotating bend mode stays the same.

Figure 6 Micrograph of Fe - 2.6 wt% N Fully transformed at 310°C (x600)

Figure 7 The hardness of austenitic iron-nitrogen alloys after ageing for 30 minutes at various temperatures.

Figure 8 Wear rates of 39MoAlCr15 in the annealed, austenitic-carbonitried, and austenitic-carbonitrided-and-aged-conditions – carbonitriding at 700°C for 1 hour in ammonia/endothermic gas with 15% residual ammonia, oil quenched, - ageing at 250°C for 2 hours

Figure 9 Wohler fatigue curves of untreated 39MoAlCr15 and 39MoAlCr15 carbonitrided at 700°C for 1 hour in ammonia/endothermic gas with 9.5% residual NH3 and oil quenched
It is likely therefore that sub-surface residual stresses play an important role in dictating the fatigue strength, especially those in the diffusion zone. The results, illustrated in figure 10, [15], show a small but real reduction in fatigue strength as a result of ageing. The corresponding residual stress data, as obtained by the X-ray diffraction technique, are illustrated for the as-quenched condition in figure 11. It can be seen that the surface nitrogen austenite exhibits a high tensile stress, but with a balancing high compressive stress at a depth of 50 µm corresponding to the formation of nitrogen martensite at the austenite/ferrite interface, due to its higher $M_S$ temperature. Ageing at 350°C for 45 minutes completely transforms the austenite to bainite leaving only a compressive stress region close to the surface, but the maximum value of 600N/mm$^2$ is lower than the original value of the untempered martensite interface, namely about 850 N/mm$^2$.

**Figure 10** The effect of ageing on the Wohler fatigue curves of austenitic nitrided 39MoAlCr15, nitrided 8 hours at 660°C and quenched; aged at 350°C for the indicated time periods

**Figure 11** Residual stress profiles for 39MoAlCr15 in the austenitic nitrided condition before and after ageing at 350°C for 45 minutes; nitrided at 660°C for 8 hours and brine quenched

**BIBLIOGRAPHY**