

NEW DEVELOPMENTS IN GASEOUS FERRITIC NITROCARBURISING BY USING HYDROCARBON GASES

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Industrial gaseous ferritic nitrocarburising processes, or shortly named „fnc“, use mainly carbon dioxide or endothermic gas as the carbon providing gas in addition to ammonia gas. Both processes have positive and negative aspects and produce somewhat different layer structures. The carbon dioxide fnc process depicts a faster layer growth yielding a thicker and more porous nitride layer, whereas the endothermic fnc process produces a nitride layer with higher carbon content and a larger proportion of the ϵ -nitride phase.

A newer variant of a fnc process uses hydrocarbons, and preferably propane or natural gas, as carbon providing gas replacing partly or totally carbon dioxide gas. This newer process uses different single or double step cycles combining the advantages of the enhanced nitrogen transfer as created by the carbon dioxide variant with the increased carbon transfer rate of the endothermic gas. This results in faster layer growth producing nitride layers with higher carbon content and a larger proportion of the ϵ -phase. This is advantageous with respect to wear resistance of the nitrocarburised components. In addition, it improves furnace productivity.

KEYWORDS: gaseous ferritic nitrocarburising, propane, nitride layer structure, ϵ/γ '-ratio, multiple step cycles, wear resistance, gear wheels, crankshafts, element concentration profiles

INTRODUCTION

With nitrocarburising, the aim is to produce a wear resistant compound layer of high ϵ -nitride content having a thickness of normally 15 – 20 μm . To achieve this, finished components are soaked for a few hours at a temperature normally between 570°C and 580°C in an atmosphere produced by feeding ammonia and a carbon supplying gas into a furnace. The first industrially developed nitrocarburising process (Nitemper®) uses a gas mixture of 50% of ammonia and 50% of endothermic gas producing in 3 to 5 hours at 570°C, a compound layer with more than 90% of ϵ -phase possessing a high carbon content up to 3 wt.-% [1].

In the middle of the 1970's, a second nitrocarburising variant was developed using exothermic gas (or nitrogen gas plus carbon dioxide) in place of endothermic gas (Nitroc®) [2].

The activating effect of the oxidizing gas CO_2 , increases the nitrogen transfer resulting in thicker compound layers (or reduced soaking times). Due to the lower carbon activity of an atmos-

phere produced with 5 vol-% of CO_2 (compared to 20 vol-% of CO as in endothermic gas), the compound layer produced by the "CO₂-process" (Nitroc®) has a lower amount of ϵ -nitride phase and contains less carbon [3] which is not beneficial for applications where wear resistance is important.

Thus from an applicational view point, the use of the "endothermic-process" is advantageous whereas from a view point of economics and of gas availability, the "CO₂-process" has a preference.

The purpose of this development programme was to create a new nitrocarburising process producing in short times sufficiently thick and wear resistant compound layers possessing a high amount of ϵ -nitride phase with a large carbon content, but not needing the availability of an endothermic gas generator.

PROCESS DEVELOPMENT

The development work is based on the utilization of a hydrocarbon gas in place of or in addition to CO_2 .

This is not the first time that hydrocarbon gases are utilized in nitrocarburising. A number of people like Prenosil [4] and Wüning [2] have shown as early as the 1960's that nitrocarburising in ammonia and a hydrocarbon gas is possible using especially gases like methane (natural gas) or propane. Their development work, however, did not lead to an industrially utilized process. It also did not have the goal of developing a new process which combines the positive effects of the "CO₂-process" with those of the "endothermic-process" without using endothermic gas and

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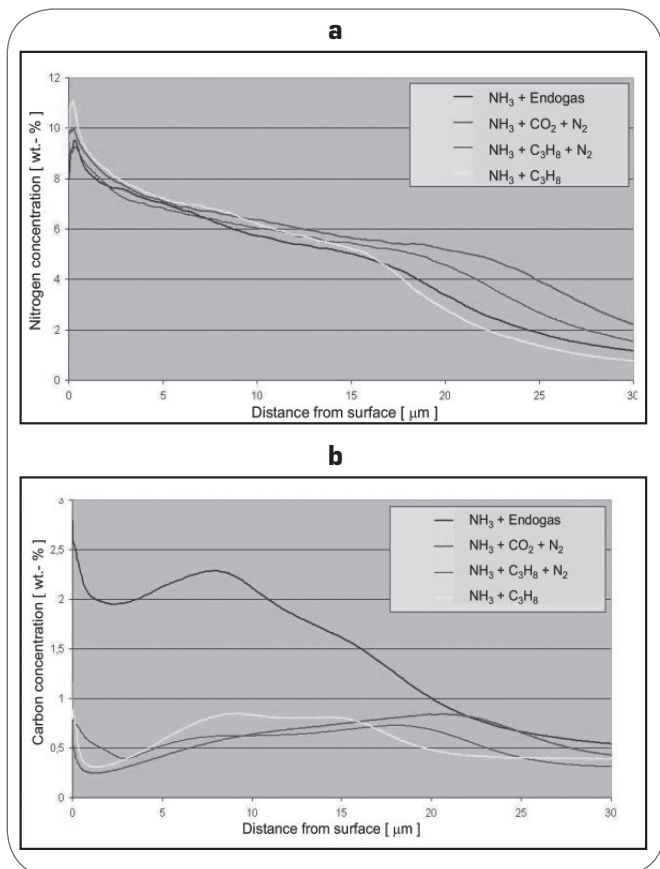


Fig. 1

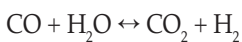
Element concentration profiles for a) nitrogen and b) carbon of steel samples of C45 (AISI 1045) after nitrocarburising (5 hrs. at 570°C) in 4 different gas mixtures with different carbon supplying gas additions. Profili di concentrazione degli elementi a) azoto e b) carbonio in campioni di acciaio C45 (AISI 1045) dopo nitrocarburazione (5 h. a 570°C) utilizzando 4 diverse miscele di gas con differenti composizioni relativamente ai gas contenenti carbonio.

which also allows the independent control of the nitriding potential K_N and of the carburising potential K_C of the nitrocarburising atmosphere.

In nitrocarburising atmospheres produced by ammonia and CO or CO₂, the respective nitriding and carburising potentials are given by

$$K_N = \frac{p(\text{NH}_3)}{p(\text{H}_2)^{3/2}} \quad \text{and} \quad K_C = \frac{p(\text{CO}) \cdot p(\text{H}_2)}{p(\text{H}_2\text{O})}$$

Thus raising or lowering the carburising potential by modifying the flow of endothermic gas has a direct influence on the nitriding potential. This influence is enhanced by the water gas reaction



which even at the low temperature of 570°C brings the 4 gas components into equilibrium. Different to this, the carburising potential in nitrocarburising atmospheres produced by ammonia and hydrocarbons like methane is defined by

$$K_C = \frac{p(\text{CH}_4)}{p(\text{H}_2)^2}$$

which makes it possible to vary the carburising potential by changing the hydrocarbon gas flow without largely affecting the nitriding potential [5].

In the first development phase of the technology, various hydrocarbon gases like the unsaturated ones

ethylene C_2H_4
propylene C_3H_6

but also the saturated ones

methane CH_4
ethane C_2H_6
propane C_3H_8

were tried. They all proved to be suitable with naturally the amount of the hydrocarbon gas addition added to the ammonia gas being in need to be adapted to the carburising capability of each hydrocarbon gas.

This second stage of process development is thus more focused on developing the cycle conditions for optimum layer growth and optimum layer properties.

For the cycle development, 3 commercially available steel types were used (C45, 16MnCr5 and 42CrMo4). Due to space and time restrictions, the results shown are mainly limited to the steel C45.

Within the scope of this development programme certain cycle data were kept constant. All loads were pre-oxidized for 60 min. at 350°C and nitrocarburised at 570°C for a total of 5 hours on temperature.

GAS COMPOSITION

Nitrogen and carbon concentration profiles as received by the GDOES-method on samples of C45 (AISI 1045) material after various gas nitrocarburising processes are shown in Fig. 1.

They demonstrate that by replacing carbon dioxide by propane in the otherwise standard "CO₂-method" produces similar nitrogen and carbon profiles as with the "CO₂-process". There are slight differences with the thickness of the compound layer being slightly smaller using propane and the carbon concentration near the surface being somewhat higher but by far not reaching the carbon concentration of 2 wt.-% and more of the compound layer produced by using endothermic gas.

Fig. 1 also indicates that leaving out the nitrogen gas and working with a pure ammonia-propane mixture achieves comparable results.

With respect to a faster growth of the compound layer it might be wise to not replace the total amount of carbon dioxide, but to work with a propane-carbon dioxide mixture. This tendency is evident in Fig. 2 with the NH₃ + C₃H₈ + CO₂ + N₂ gas mixture delivering the deepest nitrogen profile, but a somewhat lower carbon concentration in the first 2 micrometers.

Thus the positive effect of retaining some CO₂ in the gas mixture entering the furnace is the speeding up of the layer growth (higher nitrogen flux into the surface). The negative effect is the lower surface carbon concentration due to a more diluted propane gas in the gas mixture.

MULTIPLE STEP CYCLE

The best way of using the positive properties for both gases – carbon dioxide increasing the kinetic of the nitrogen transfer and propane increasing the carbon activity – is not to mix the

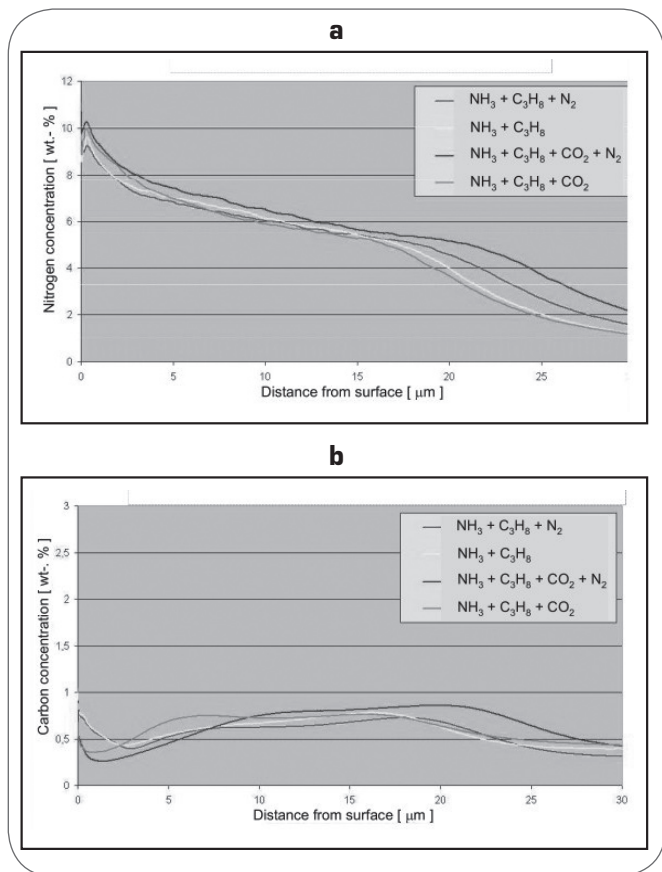


Fig. 2 *Element concentration profiles for a) nitrogen and b) carbon of C45-steel nitrocarburised (5 hrs. at 570°C) in gas mixtures with propane and propane plus carbon dioxide.*
 Profili di concentrazione degli elementi a) azoto e b) carbonio in acciaio C45 nitrocarburato (5 h. a 570°C) utilizzando miscele di gas con propano e propano più biossido di carbonio.

2 gases but to apply them separately in 2 different steps of the nitrocarburising cycles similar to a process developed in the early 1980's by F.W. Eysell [3].

The respective concentration profiles in Fig. 3 indicate that a first step of 1 hour (at 570°C) with ammonia and carbon dioxide is sufficient to achieve the kinetics improvement.

They also show that the longer the cycle step using propane is (4 hrs. better than 2.5 hrs.), the higher the surface carbon concentration. Also a very small addition of carbon dioxide to the propane cycle step does not seem to have a negative influence.

Nitrogen gas can be used in these 2-step cycles but has basically no influence. Results without nitrogen gas are just as good. The maximum surface carbon content of the 2-step propane- CO_2 method is in the range of 1.0 wt.-% and is thus twice as high as the 0.5 wt.-% of the pure CO_2 -method.

INFLUENCE OF THE STEEL GRADE

There is as expected an influence of the alloying content of the steel on the element concentration and on layer thickness. Fig. 4 shows the results for the 3 steels C45, 16MnCr5 and 42CrMo4.

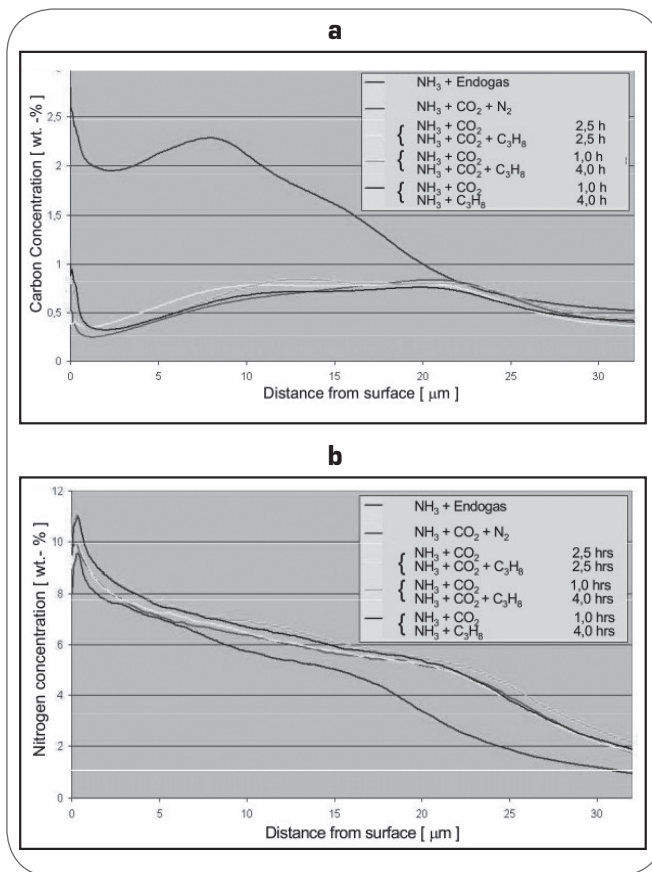


Fig. 3 *Element concentration for a) nitrogen and b) carbon of C45-steel nitrocarburised in 2 single step and 3 double step cycles.*
 Concentrazione degli elementi a) azoto e b) carbonio in acciaio C45 nitrocarburato in cicli a 2 singoli passi e 3 passi doppi.

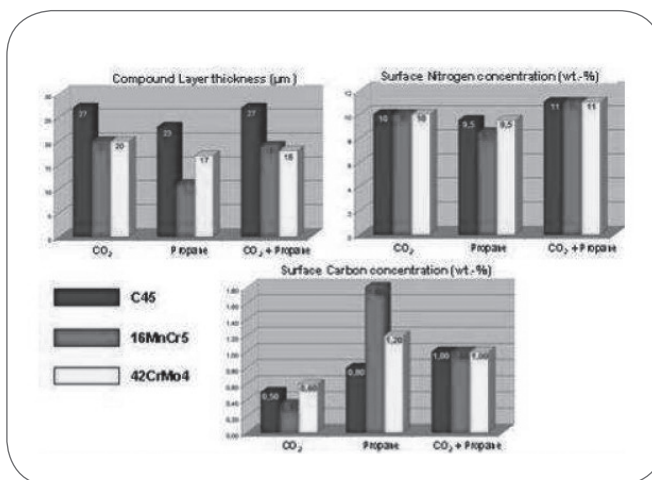


Fig. 4 *Influence of the carbon providing gas and the type of steel on compound layer thickness, surface nitrogen and surface carbon content.*
 Influenza del gas che fornisce carbonio e del tipo di acciaio sullo spessore dello strato e sul contenuto superficiale di azoto e di carbonio.

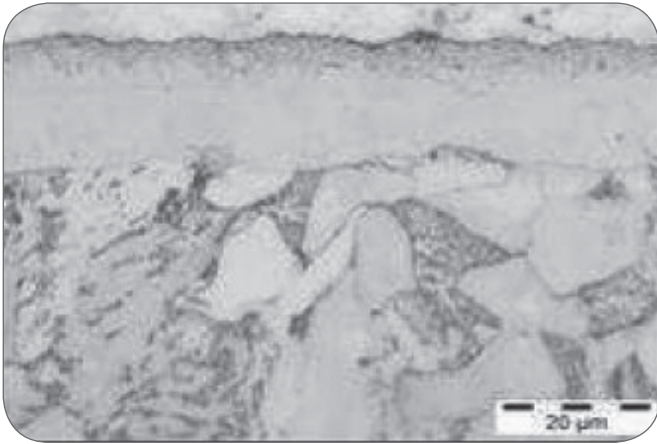


Fig. 5 *Micrograph of compound layer on the steel 16MnCr5 after nitrocarburising in a 2-step cycle using propane and CO₂.
Micrografia dello strato superficiale su acciaio 16MnCr5 dopo nitrocarburaione con un ciclo in 2-passi, utilizzando propano e CO₂.*

Property	Specification	Average values achieved after the	
		CO ₂ -Process	Propane-Process
surface hardness (HV10)	>300	317	323
compound layer thickness (μm)	>12	20	18
total nitriding depth (mm)	≥0.9	0.95	1.0
brittleness (grade ^{*)})	1-2	2	1.5
porosity (grade ^{*)})	1-2	1	1
nitride precipitations (grade ^{*)})	1-2	1	1
wear after heavy duty pilote test	no wear visible on journals	distinct wear marks visible	no wear visible
ε-phase/γ'-phase	---	4:1	11:1

* = chin. standard

Tab. 1 *Specifications for nitrocarburising of diesel engine crankshafts plus results achieved after nitrocarburising with the CO₂-process and with the propane process [6].
Specifiche di nitrocarburaione di un albero a gomito di un motore diesel e risultati ottenuti con il procedimento a CO₂ e con quello a propano.*

It becomes clear that surface nitrogen content is not at all influenced by the steel grade and only very little by the different carbon providing gases delivered to the furnace. The nitriding potential is about 2.0 for the CO₂-process and for the propane-process. It is almost double (4.0) for the 2-step propane-CO₂ process, which accounts for the increase in surface nitrogen content.

Compound layer thickness decreases as expected with increasing steel alloy content, whereas surface carbon content seems to increase somewhat with the alloying content but strongly with the addition of propane to the gas. This is because the carbon potential of a propane containing nitriding atmosphere is about 3 times higher as compared to the CO₂-process (0.16 versus 0.05). The micrograph of a compound layer as produced by nitrocarburising the steel 16MnCr5 using the new 2-step method with propane and CO₂ (for 5 hours at 570°C) is depicted in Fig. 5.

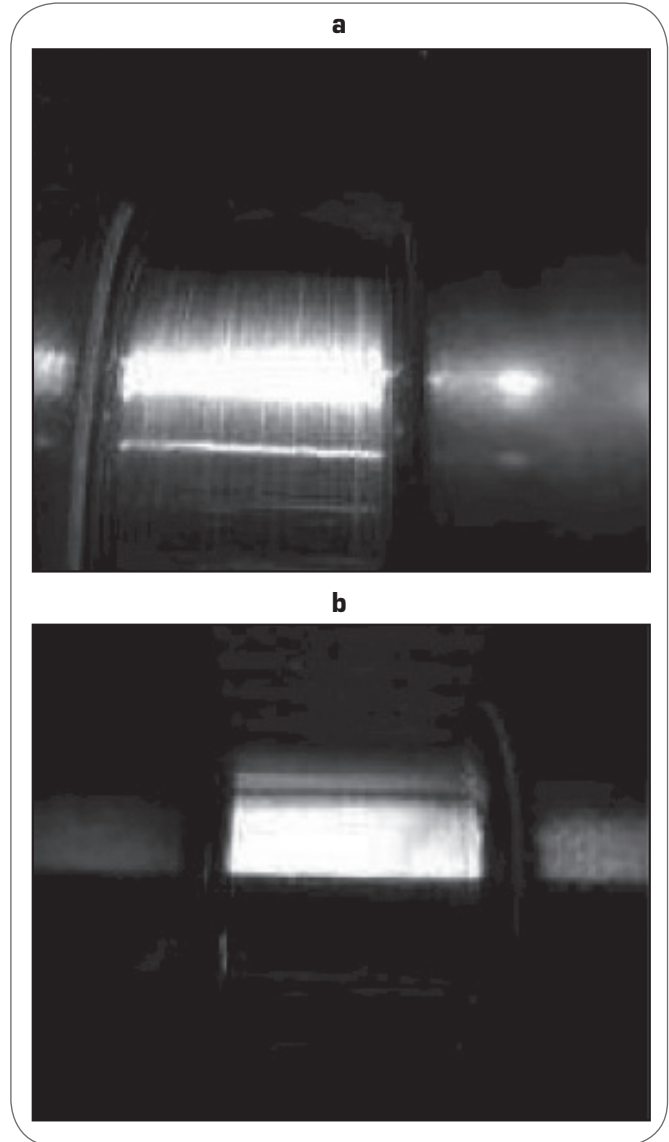


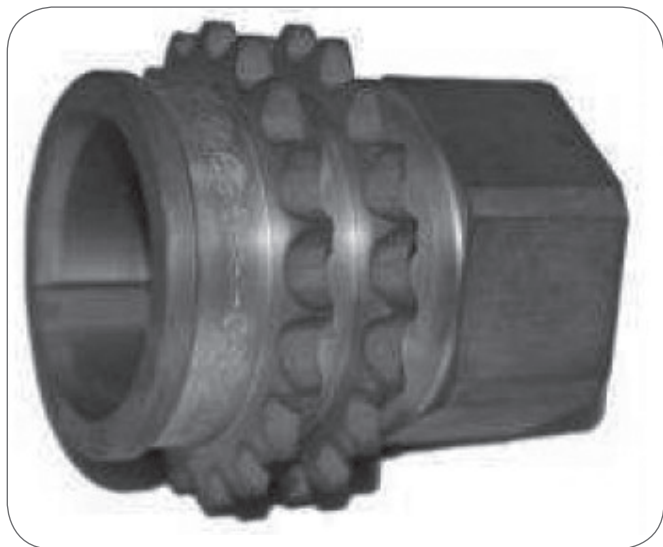
Fig. 6 *Surface appearance of the journals of crankshafts nitrocarburised with a) the CO₂-process and b) the propane-process [6].
Aspetto superficiale di un supporto di albero a gomito nitrocarburaione utilizzando i processi a) con CO₂ e b) con propano[6].*

The compound layer thickness is almost 20 μm and shows a low porosity in the first 5 to 6 μm.

INDUSTRIAL APPLICATIONS

Crankshafts of high powered diesel engines (weighing 100 kg and more) are subjected to high torsional stresses but also high wear loading on the surfaces of the journals. They are produced from C45 steel, forged, normalized and nitrocarburised. Their specification with respect to the nitrocarburising results is shown in Tab. 1.

The standard CO₂-nitrocarburising process (50 vol-% ammonia, 45 vol-% nitrogen gas, 5 vol-% carbon dioxide) achieved all values of the specification expect for passing the heavy duty pilot test. All crankshafts treated this way and put through the pilot test with high loading failed and showed



▲
Fig. 7

Drive sprocket made of 16MnCr5 steel.

Ruota dentata in acciaio 16MnCr5.

clear wear marks on the journals.

In order to overcome this problem, the manufacturer of the diesel engines raised the nitriding potential of the atmosphere by 1) omitting the nitrogen gas and increasing the ammonia content and 2) working with a higher total gas flow to the furnace.

Both measures were not successful. Once it was established that the low carbon content of the compound layer and the high amount of γ' -nitride phase could be the cause of the problem, the new propane process was tried using ammonia and propane without nitrogen gas. This lifted the carbon concentration in the compound layer and especially the ratio of ϵ/γ' from 4 : 1 to 11 : 1 (tab. 1).

The result was a flawless surface appearance of the crankshafts' journals after the heavy duty pilot test (Fig. 6) [6].

There are not too many occasions that a manufacturer of a component and a user of the nitrocarburising process recognizes the importance of the carbon content and especially of the ϵ/γ' -ratio of the compound layer on the wear behaviour of the respective



▲
Fig. 8

Gear wheels of 42CrMo4 material nitrocarburised in ammonia plus methane.

Ingranaggi in acciaio 42CrMo4 nitrocarburati con ammoniaca più metano.

component.

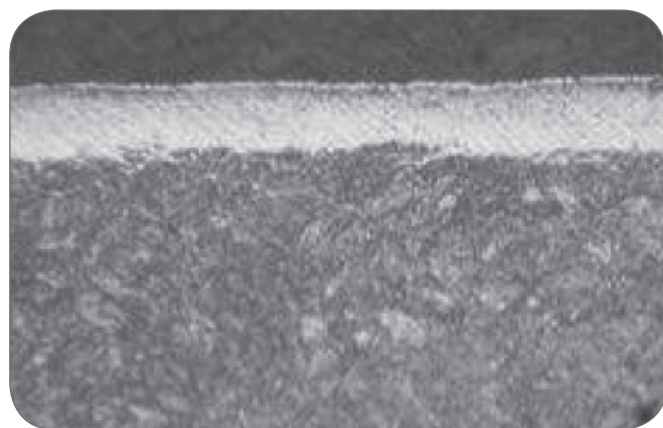
One car manufacturer obviously does. He prescribes in the nitrocarburising specification of the sprocket of Fig. 7 among others the achievement of a minimum ϵ/γ' -ratio of 7 : 1 (Tab. 2).

The standard CO₂-process was not able to fulfil this requirement. The propane process far over exceeded this goal and has been in use as a standard process for this part since some years.

As mentioned earlier, propane is not the only hydrocarbon gas to be used. Others as ethane, methane, ethylene or propylene work as well.

A commercial heat treater in Italy has been working with a 2-step cycle method for some time now using ammonia and methane (without nitrogen) in the second step. Naturally, due to the lower carbon availability of methane, the amount of methane in the gas mixture needs to be higher than the usual 4 to 6 vol.-% as in the case of propane. Fig. 8 shows typical gear wheels of 42CrMo4 treated with this method.

The gears receive a compound layer of 15 – 17 μm after a 2-step cycle of 5 hours at 570°C (Fig. 9).



▲
Fig. 9

Compound layer of gear wheel (42CrMo4) after nitrocarburising with ammonia and methane.

Strato ottenuto su un ingranaggio (42CrMo4) dopo nitrocarburazione con ammoniaca più metano.

Property	Specification	CO ₂ -process	Propane-process
surface hardness	min. 620 HV1	achieved	achieved
nitriding case depth	min. 0.30 mm	achieved	achieved
thickness of c.l.	10 – 20 μm	achieved	achieved
ϵ/γ' -proportion	>7 : 1	not achieved 5.6 : 1	achieved 15.6 : 1

▲
Tab. 2

Nitrocarburising specification for the drive sprocket of 16MnCr5 steel and results achieved using the CO₂-nitrocarburising process and the propane-process.

Specifiche di nitrocarburazione per una ruota dentata in acciaio 16MnCr5 e risultati ottenuti con il procedimento a CO₂ e con quello a propano.

CONCLUSIONS

The addition of hydrocarbon gases to the nitrocarburising atmosphere replacing partially or totally the carbon dioxide gas increases the carburising capability of the nitrocarburising atmosphere. This results in a higher surface carbon concentration of the ϵ -layer and a larger ϵ/γ' -nitride ratio yielding a remarkably improved resistance to wear under high loading.

A 2-step procedure makes use of the kinetics improving capability of carbon dioxide in the first cycle step and the increased carbon flux of the hydrocarbon gas in the second cycle step. This has the advantage of producing thick compound layers with a high carbon concentration in a comparatively short cycle.

Growing industrial applications in the engine and gear box manufacturing industry in the last few years clearly demonstrate the rising of this new technology.

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ABSTRACT

NUOVI SVILUPPI NELLA NITROCARBURAZIONE FERRITICA IN FASE GASSOSA MEDIANTE L'UTILIZZO DI GAS DI IDROCARBURI

Parole chiave: trattamenti termici, processi

I processi industriali di nitrocarburazione ferritica, chiamati anche "FNC", impiegano, come fonte del carbonio, principalmente biossido di carbonio oppure gas endotermici, da aggiungere ai vapori di ammoniaca. Entrambe le soluzioni presentano aspetti positivi e negativi, e danno origine a strati con strutture leggermente diverse. Con il processo FNC con biossido di carbonio si ottiene una crescita più veloce dello strato di nitruro, che risulta essere anche di maggiore spessore e più poroso, mentre il processo FNC endotermi-

co produce uno strato di nitruro con maggiore contenuto di carbonio e una maggiore concentrazione della fase nitruro ϵ .

Una nuova variante del processo FNC utilizza degli idrocarburi come gas che forniscono carbonio - preferibilmente propano o gas naturale - sostituendo parzialmente o totalmente il biossido di carbonio. Questo nuovo processo, che utilizza cicli a passo singolo o doppio, abbina i vantaggi del migliore trasferimento di azoto, che si è visto essere proprio del processo con biossido di carbonio, con la maggiore velocità di trasferimento di carbonio, caratteristica del caso di impiego di gas endotermici. Ciò permette di ottenere una crescita più veloce dello strato di nitruro, caratterizzato inoltre da un elevato contenuto di carbonio e da una maggiore presenza della fase ϵ . Questo risulta essere vantaggioso per quanto riguarda la resistenza all'usura dei componenti nitrocarburati, migliorando inoltre la produttività dell'impianto.