

# The behaviour of decarburized layers in steel nitriding

I. Calliari, M. Dabalà, E. Ramous, M. Zanesco, E. Gianotti

*Samples of quenched and tempered 40CrMo4 steel, previously surface decarburized at different depths, have been submitted to gaseous nitriding. The surface layers after decarburization and nitriding was examined by optical microscopy (OM), scanning electron microscopy (SEM) and microhardness tests.*

*The distribution of iron nitrides in the diffusion layer was analyzed by X-ray diffraction (XRD). The nitrogen and carbon profiles in the diffusion layers were determined by scanning electron microscope equipped with a wavelength dispersive spectrometer (EPMA-WDS).*

*For all the specimens, the highest hardness values only change slightly with increasing time and temperature of decarburization, while case hardness depths decrease.*

*In all the specimens, the nitriding depth, as determined by the nitrogen profile, is larger than the one determined by the hardness profile.*

**Key words:** decarburization, nitriding, steel, 40CrMo4

## INTRODUCTION

The surface microstructure on nitriding steels has been widely investigated and discussed in several papers (1-4). The nitriding process develops a zone which can be subdivided into a compound (white) layer, with carbo-nitrides, and an underlying diffusion layer. The compound layer is formed by nitrides and carbonitrides, while interstitial nitrogen and alloy forming elements (Cr, Mo, Al, and V) nitrides are present in the diffusion layer.

The nitrided layers structure depends on the interaction between the diffusional nitrogen and original steel microstructure, normally ferrite and carbides, caused by the tempering heat treatment, which is usually performed on steel before nitriding. A special role is played by the transformation of Cr carbides to Cr nitrides (5), so the C may diffuse interstitially from the diffusion layer to the compound layer, where it forms carbides. This transformation explains why the final microstructure of nitrided steels depends not only on the C content but also on the C distribution (6) in the prior steel microstructure. The nitriding treatment modifies the carbides and C distribution which then affects also the hardness profile in the N-enriched layer (7). Occasionally, in industrial practice, the nitrided work pieces can present some surface decarburization due to previous heat treatments. The behaviour of nitrided samples after a controlled surface decarburization has been examined in this study.

The main differences between decarburized and non-decarburized layers are obviously the lower carbides content and the larger ferrite grain sizes in the former. The low carbide content determines that nitrides may form by precipitation from ferrite and not by carbides decomposition. The large ferrite grain size implies that the grain boundary nitrogen diffusion increases and the grain boundary nitrides precipitation is enhanced.

Moreover, the study could give more information about the

effect of pre-oxidation treatments, often suggested to improve nitrogen take-up, and about the redistribution of carbon observed during nitriding.

## EXPERIMENTAL PROCEDURES

The specimens have been obtained from a bar (diameter 28 mm) of commercial steel 4140 quenched (in oil at 840°C) and tempered (2 h at 600°C).

Six different thermal cycles, aimed at obtaining surface decarburization, were conducted in the experimental condition reported in table 2.

After metallographic preparation, the cross-sections of the specimens were etched with Nital 4% in order to characterize the structure and evaluate the decarburized thickness through optical microscopy.

The decarburized specimens were submitted to the following nitriding treatment: all the specimens were heated at 350°C in air, from 350°C to 400°C in N<sub>2</sub> and then kept at 400°C for 30 minutes in N<sub>2</sub>, from 400°C to 510°C in N<sub>2</sub> and then kept at 510°C for 72 h with a NH<sub>3</sub> dissociation of 25%.

Steel	Composition %						
	C	Mo	Mn	Cr	Ni	Cu	Si
4140	0,432	0,2	0,85	1,148	0,122	0,267	0,243

Table 1 – Composition of the nitrided steel.

Tabella 1 – Composizione dell'acciaio.

Sample	Thermal cycle	Cooling
1	3 h 800°C	Air
2	4 h 800°C	Air
3	3 h 840°C	Air
4	4 h 840°C	Air
5	3 h 900°C	Air
6	4 h 900°C	Air

Table 2 – Decarburization heat treatment.

Tabella 2 – Trattamenti per ottenere gli strati decarburati.

I. Calliari, M. Dabalà, E. Ramous, M. Zanesco  
DIMEG Department of Innovation in Mechanics and Management, Padova

E. Gianotti  
Heat Treatments Ferioli & Gianotti Spa, Rivoli (TO)

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The cross-sections of the nitrided specimens were etched with Nital 4% to observe the microstructure and subsequently etched with Murakami in order to evaluate the distribution of carbides, by light and SEM microscopy. Microhardness profiles were performed using a load of 200g. The concentration profiles of nitrogen and carbon in the nitride layers have been determined by GDOS spectrometry on the surface layers, and by the JEOL-JXA microprobe (with spectrometers 4 WDS). A Siemens D5000 X-ray diffractometer with Cu K $\alpha$  radiation was used to examine the phases of white surface layers.

RESULTS AND DISCUSSION

1. Decarburized samples

Table 3 reports the values of decarburized depths, surface hardness after nitriding and effective depth of nitriding ; it is evident that the decarburized thickness increases with time and temperature of heat treatment.

In fig.1 an example(sample 2, 800°C,4h) of the microstructure of the decarburized surface layer is reported. Particularly in the samples n. 5 and 6, the decarburization produces a completely ferritic microstructure with coarse grains. The increase in ferrite grain size is important because, during the nitriding process, the nitrogen diffuses preferentially along the grain bounda-

Sample	Depth of Decarburising ( $\mu\text{m}$ )	Surface hardness after nitriding ( $\text{HV}_{0.5}$ )	Effective depth after nitriding ( $\mu\text{m}$ )
0	0	841+-12	481
1	150	817+-10	476
2	290	836+-16	470
3	300	810+-12	444
4	310	841+-12	415
5	460	814+-14	436
6	490	817+-16	388

Table 3 – Decarburized depths, surface hardness after nitriding and effective depth of nitriding.

Tabella 3 – Spessori degli strati decarburati, durezza superficiale dopo nitrurazione e spessori efficaci di nitrurazione.

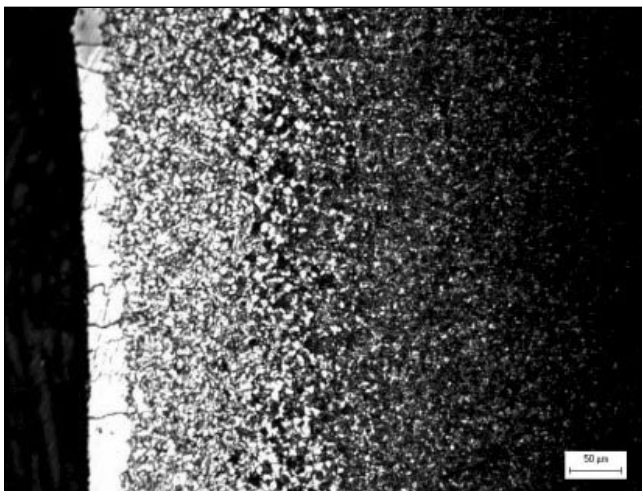


Fig. 1 – Optical micrograph of sample 2 (800°C,4h).

Fig. 1 – Microstruttura del campione 2 dopo decarburazione (800°C, 4 ore).

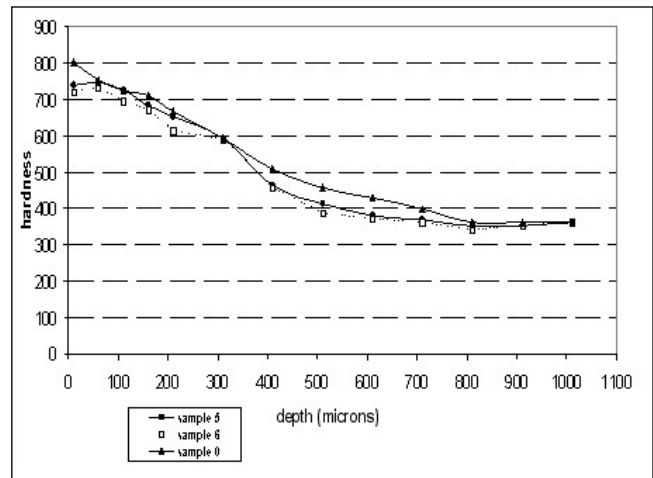


Fig. 2 – Hardness profiles of samples 5,6 and 0.

Fig. 2 – Profili di microdurezza dei campioni n. 5, 6 e 0.

ries. As the grain size increases, the nitrogen gradient concentration between grain core and grain boundaries may increase and the nitrides precipitation along the grain boundaries is favoured.

2. Nitrided samples

2a. Surface hardness

The surface hardness values measured after nitriding are reported in the 3<sup>rd</sup> column of table 3. The values are the mean of 10 measurements randomly taken on the surface. Samples from 1 to 6 have been heat treated as indicated in table 2, while sample 0 has only been nitrided in the same experimental conditions of 1-6 but not decarburized.

All the hardness values are higher than the 600HV required by the standard. The surface hardness is not affected by the different rate of decarburization, as sample 0 has the same hardness as the others. High nitrogen enrichment in the compound layer probably compensates the carbon loss and the resulting hardness can only be determined by nitriding.

2b. Hardness profiles

Fig. 2, reports the microhardness profiles of samples 5 and 6, superimposed with profiles of sample 0. All curves have the typical trend of nitrided steels, showing a decreasing hardness from surface to core. There is no sharp transition in the hardness values from the compound layer to the diffusion zone and this can be attributed to the high hardness levels achieved in the diffusion zone after the long nitriding process and despite the carbon loss. The effect of decarburization can be evaluated by comparing the profiles of samples 1-6 with the profile of sample 0 in the diffusion zone. The hardness values of sample 0 are slightly higher than those of samples 1-6; the differences are in the range of 10-20HV and decrease as the depth increases. This difference can be explained by the lower hardness values of the decarburized samples where a limited amount of carbides is present. The consequence of the lower profile is that the effective case depth after nitriding decreases. The last column of table 3 reports the effective depth values measured on all the samples, the hardness of 460HV has been achieved at depths varying from 390 to 480microns. The value of 480microns has been measured in sample 0, while sample 6 (having the deepest decarburization) has the minimum depth of 390 microns.

2c. Microstructure

Optical and electronic microscopy metallographic investigations were performed to observe the influence of decarburization on the microstructure after nitriding. The results for

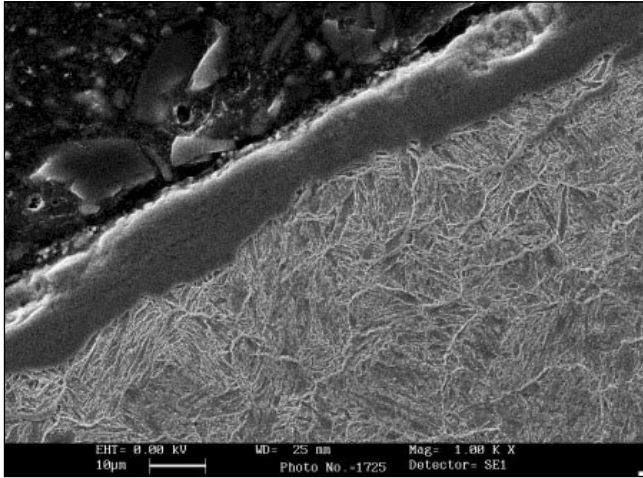


Fig. 3a – SEM micrograph of sample 0.

Fig. 3a – Micrografia SEM del campione 0.

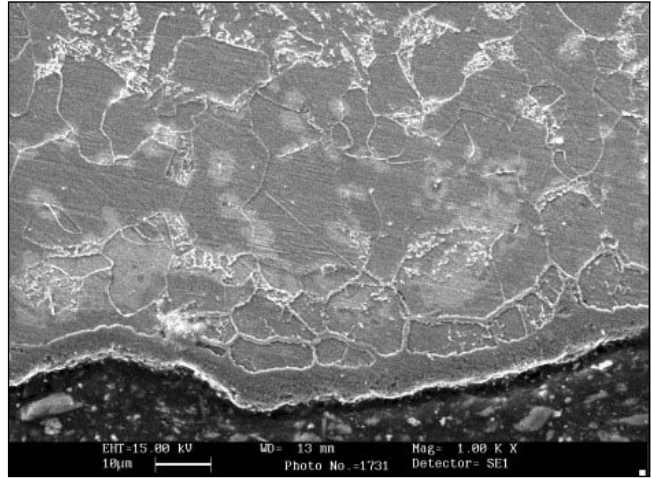


Fig. 3b – SEM micrograph of sample 5.

Fig. 3b – Micrografia SEM del campione 5.

sample 0 (nitriding without decarburising) and sample 5 (850°C, 4h and nitriding) are presented in figs. 3a and 3b. The compound layers and diffusion zone with grain boundary precipitation are visible.

The main features of the white layer in the decarburized samples can be summarized as follows:

- It is about 30% thinner than in simply nitrided sample,
- It appears unhomogeneous, with many voids, diffuse porosity and some cracks and the outer surface is friable with scaling, mainly in the deeply decarburized samples.

In the diffusion zone, dark precipitates formed at the grain boundaries. Fig.4 reports the SEM-BSE micrograph taken without etching on sample 3 cross section (800°C, 30'). The precipitation starts beneath the white layer and grows for about 10 microns towards the diffusion layer. This morphology is more evident in highly decarburized samples, where the high temperature and holding time of heat treatment determines grain growth. After this heat treatment the surface base material was partially ferritic and the ferrite volume fraction increased with temperature and holding time. After nitriding, no significant amount of ferrite was detected in the low decarburised samples. This means that interstitial diffusion of N and C occurs, both at grain boundaries and inside the grains, resulting in a quite homogeneous microstructure.

On the other hand, in the diffusion zone of highly decarburised samples some ferritic grains still remain. It means that in these samples the diffusion mechanism occurs mainly at grain boundaries and despite the long nitriding time, the interstitial elements C and N were not able to diffuse up to the inner zone of the ferritic grains.

*2d. Composition and microstructure of nitrided layers*

The concentration profiles of carbon and nitrogen in cross-sections of decarburised and nitrided samples were determined by wave-length dispersive electron microprobe analysis (WDS-EPMA).

The results, obtained from samples 0 and 5 (900°C, 3h, nitriding), are given in figs. 5a and 5b, along with the hardness profiles for comparison. The C and N concentrations are expressed as Count/sec/mA.

The higher nitrogen concentrations, measured on the surface of sample 0, are caused by the compound layer, which is less porous and more homogeneous than in samples 3 and 5.

In all the samples the nitrogen content decreases from surface to core; with the mean concentration in the diffusion zones of samples 3 and 5 slightly lower than in sample 0. In all specimens the nitriding depth as determined by the nitrogen profile is larger than that determined by the hardness

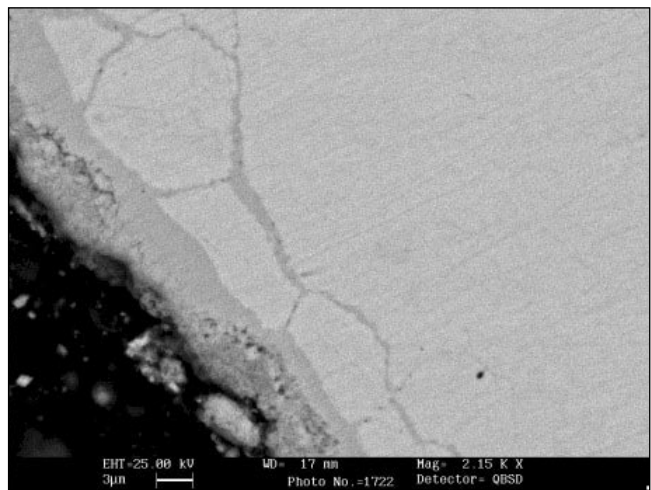


Fig 4 – SEM-BSE micrograph of sample 3.

Fig. 4 – Micrografia SEM-BSE del campione 3.

profiles, arriving at about 700microns.

The carbon profiles are obviously more affected by the decarburising process. The peaks in the carbon concentrations in the diffusion layer of sample 0 indicate the presence of carbides. The carbon profiles in the diffusion zone of samples 3 and 5 show the different depth of decarburised layer. Some peaks in profile of sample 3 indicate the presence of a few (small) carbides and the profile of sample 5 indicates a complete absence of C beneath the surface. The carbon concentration profiles of both samples correspond to the depth of the decarburized layers evidenced by the optical microscopy.

The carbon and nitrogen contents in compound layers have been examined by the Glow Discharge Optical Spectrometry (GDOS), to a depth of about 70 microns with nanometric spatial resolution.. The profiles of C and N obtained on samples 0 and 6 are reported in fig.6 The GDOS profile of carbon in sample 0 after nitriding show that carbon is absent for about 10 microns, which correspond to the white layer, and increases with depth to reach the base alloy concentration of 0.40%.The carbon loss associated with nitriding is well known: during the nitriding treatment the carbon diffuses to the core as well as to the surface.

The GDOS profiles of C and N in decarburized samples show that carbon is absent in the analysed depth (about 70 microns). Instead, there is a higher nitrogen surface concentration (more than 1%), compared to that observed in the sample without

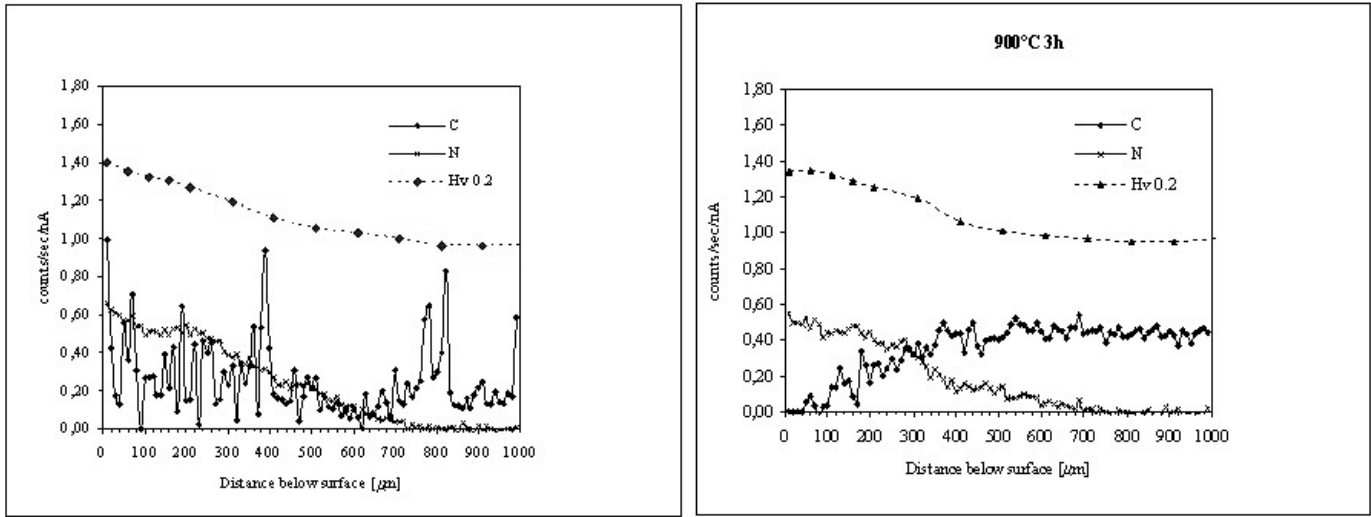


Fig. 5a (left) and fig. 5b (right) – Nitrogen and Carbon EPMA-WDS profiles and hardness profile of sample 0 (left) and of sample 5 (right).  
 Fig. 5a (sinistra) e 5b (destra) – Profili di microdurezza e delle concentrazioni di carbonio e azoto ottenuti con EPMA-WDS del campione 0 (a sinistra) e 5 (a destra).

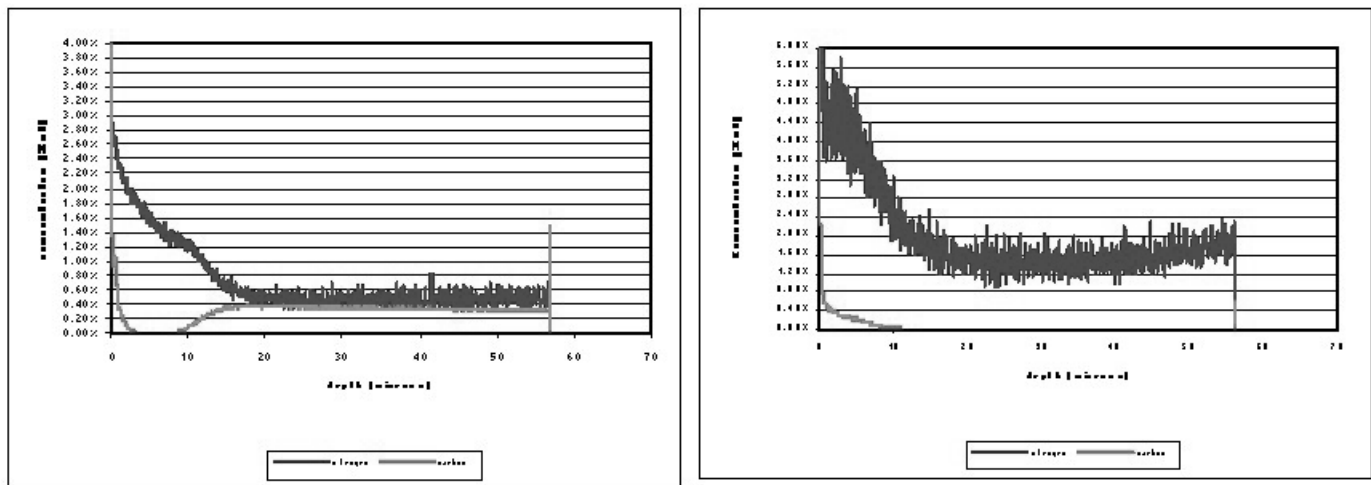


Fig.6 – GDOS profiles of N and C taken on the compound layers of sample 0 (left) and 6 (right).  
 Fig. 6 – Profili di concentrazione del carbonio e dell' azoto nello strato di composti, ottenuti con GDOS nei campioni 0 (a sinistra) e 6 (a destra).

decarburation, followed by a smooth decrease to a value which remains constant in the examined layer.

This higher nitrogen concentration in the surface layers, both in the white layer and beneath this layer, appears as the main difference, when compared with the non-decarbured sample. The nitrogen content of the white layer in the sample 0 is about 0,4%, and arrives to the value of 1, 5% in the more decarbured samples. There is a similar difference in the inner layer, beneath the compound one. These data suggest that the surface decarburation favours the diffusion of nitrogen, mainly along the grain boundaries

These results have been confirmed by the metallographic investigation, which evidenced that in decarbured samples the nitrogen compounds precipitate at grain boundaries as needle-like particles, coarser in the more carbon depleted samples.

The GDOS measurements evidenced also the surface enrichment in Si, Mo and Cr in the decarbured and nitrated samples. The GDOS profiles indicate that the Si, Mo and Cr enrichment is limited to the 5-10 microns of the white layer. The Si and Mo concentrations measured at the surface are about 2 %, while the Cr concentration reaches 7-9%. It has been verified that surface enrichment occurs during the decarburation heat treatment and is not affected by nitrating. Fig.7 reports the Si, Mo and Cr profiles obtained on the decarbured, not nitrated, sample 5.

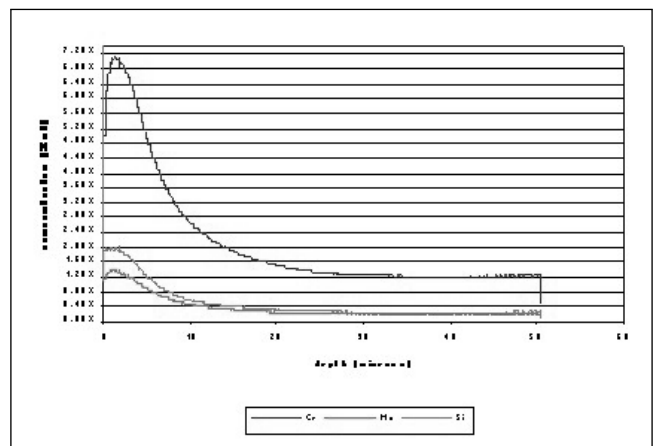


Fig.7 – GDOS profiles of Mo,Si,Cr on sample 5.  
 Fig. 7 – Profili di concentrazione di Mo, Si e Cr ottenuti con GDOS nel campione 5.

The occurrence of Si, Mo and Cr surface enrichment can be easily explained by their high oxygen affinity which favours their outward diffusion during the air decarburation treatment.

The surface layers constitution was investigated with XRD: in the white layer the presence of nitrides  $\epsilon$  ( $\text{Fe}_3\text{N}$ ) e  $\gamma$  ( $\text{Fe}_4\text{N}$ ) was confirmed. The volume fraction of  $\epsilon$  is about 60% in all samples; a moderate increase of  $\gamma$  fraction was detected in the more deeply decarburized samples.

CONCLUSIONS

The effects of decarburisation on properties and structure of nitrated surface layers in the 40Cr4Mo steel can be summarized as follows:

1. The surface hardness is not affected and the hardness profiles of decarburised samples are slightly lower than the profile of the only nitrated sample.
2. In all samples the nitrogen content decreases from surface to the bulk. In the previously decarburised samples the nitrogen concentration is significantly higher in the first surface layers and slightly lower in the diffusion zones, as compared with the non-decarburised sample.
3. In all specimens the nitriding depth as determined from the nitrogen profile is larger than that determined from the hardness profiles, arriving at about 700 microns.
4. The white layer of nitrated and decarburised samples is more porous and friable, with coarser grains than in the non-decarburized samples.

5. The thickness of the white layer decreases as the decarburisation increases.
6. The main effect of the previous decarburization on the nitrated layers seems to be the modification of the morphology and composition of the compound layer.
7. The actual effects of carbon loss on microstructure and hardness after nitriding are probably compensated by the strong nitriding conditions of our experiment, which favour the growth and development of compound layers.

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A B S T R A C T

COMPORAMENTO DI STRATI SUPERFICIALI DECARBURATI SOTTOPOSTI A NITRURAZIONE

Parole chiave: decarburazione, nitrurazione, acciaio 40CrMo4

Normalmente il trattamento di nitrurazione viene eseguito su acciai bonificati, quindi con una struttura costituita da martensite rinvenuta e carburi. L'arricchimento in azoto per diffusione prodotto dalla nitrurazione modifica questa microstruttura: in particolare i carburi di cromo vengono trasformati in azoturi, liberando il carbonio che diffonde sia nella zona di diffusione, sia verso lo strato superficiale di composti. Quindi la nitrurazione non solo arricchisce lo strato superficiale in azoto, ma modifica anche la distribuzione del carbonio: tutto questo influisce sul profilo e sui valori di durezza degli strati nitrurati. Poiché nella pratica i trattamenti eseguiti prima della nitrurazione occasionalmente possono provocare una certa decarburazione nella zona superficiale dei pezzi, è stato esaminato il comportamento durante la nitrurazione di strati superficiali volutamente decarburati in un tipico acciaio da bonifica, l'AISI 4140 (tabella 1). La decarburazione è stata ottenuta mediante riscaldamento in aria a temperature comprese fra 800 e 900°C (tabella 2). Gli strati decarburati (figura 1), per spessori compresi fra 150 e 300 micron, presentavano una struttura con grossi grani di ferrite ed ovviamente assenza di carburi. La nitrurazione è stata eseguita a 512°C per 72 ore, con ammoniaca dissociata al 25%. I campioni trattati sono stati esaminati con le usuali tecniche metallografiche, spettrometria GDOS, microsonda WDS e diffrazione X. Dopo nitrurazione, la durezza superficiale dei campioni decarburati è solo lievemente inferiore a quella del campione solo bonificato, e comunque largamente superiore al valore minimo richiesto (tabella 3). Anche i profili di microdurezza (figura 2), mostrano solo una lieve diminuzione rispetto ai valori riscontrati sul campione non decarburato. Però questa diminuzione si mantiene per tutta lo spessore dello strato trattato e di conseguenza i campioni decarburati presentano una profondità efficace di nitrurazione inferiore (tabella 3). Tale diminuzione aumenta con l'aumentare della profondità di decarburazione. Questo effetto è certamente dovuto alla minore concentrazione di car-

bonio negli strati decarburati. Nella microstruttura degli strati nitrurati dopo decarburazione (figura 3 a, b e c) le maggiori differenze riguardano lo strato di composti, che ha uno spessore inferiore di circa il 30%. Inoltre questo strato appare eterogeneo, con molti vuoti, porosità e fessurazioni, che lo rendono friabile e poco resistente allo scagliamento. Nello strato di diffusione si notano evidenti fenomeni di precipitazione a bordo grano, che confermano la prevalente diffusione dell'azoto lungo i bordi grano. Tuttavia grani di ferrite sono presenti solo nei campioni maggiormente decarburati. Con analisi WDS-EDS sono stati tracciati i profili di concentrazione del carbonio e dell'azoto nello strato di diffusione (figura 5 a e b). Nei profili del carbonio si notano i picchi dovuti ai carburi nel campione non decarburato, mentre il carbonio è praticamente assente nel campione decarburato. Invece in tutti i campioni l'andamento del profilo dell'azoto presenta una diminuzione graduale, che arriva a profondità superiori a quelle corrispondenti all'aumento della durezza, a conferma che piccole concentrazioni di azoto possono avere solo scarsa influenza sulla durezza. Il contenuto di carbonio e azoto nello strato superficiale di composti è stato invece analizzato con la spettrometria GDOS (figura 7 a e b). Per il carbonio i risultati mettono in evidenza la ovvia assenza di carbonio nello strato superficiale dei campioni decarburati, mentre nel campione solo nitrurato, il carbonio è assente solo fino a circa 10 micron, a conferma dell'effetto di decarburazione superficiale prodotto dalla nitrurazione. L'andamento dell'azoto evidenzia invece che lo strato di composti nei campioni decarburati ha una concentrazione di azoto sensibilmente più elevata, circa 1,5%, rispetto al campione solo nitrurato, dove l'azoto arriva allo 0,4%. Nei campioni decarburati anche lo strato di diffusione più interno, presenta un'analogo maggiore concentrazione di azoto. Ciò sembra indicare che la decarburazione favorisce una maggiore diffusione dell'azoto, probabilmente soprattutto lungo i bordi grano. Le analisi GDOS hanno anche rivelato un arricchimento superficiale in molibdeno, silicio e cromo (figura 7), tutti elementi in lega con elevata affinità per l'ossigeno. Tale arricchimento è giustificato da una diffusione preferenziale di questi elementi verso la superficie, durante il trattamento di decarburazione ossidante.