

# Microstructure of a Nitrided Steel Previously Decarburized

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**In this study the effects of a surface-controlled decarburization on the structure of a nitrided steel are analyzed. Samples of a quenched and tempered 42CrMo4 steel were decarburized by heating in air at different depths and submitted to gaseous nitriding. After decarburization and nitriding, the microstructure of surface layers was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). The nitrogen and carbon profiles in the diffusion layers were determined by SEM equipped with a wavelength dispersive spectrometer (EPMA-WDS) and by glow discharge optical spectrometry (GDOS). The effect of nitriding was determined by microhardness measurements. Our results indicate that a previous decarburization only slightly affects the surface hardness, but reduces the conventional nitriding depth. The decarburization also favors the nitrogen take-up and produces increased nitrogen concentrations in the compound layer and in the narrow zone beneath it.**

**Keywords** decarburization, glow discharge optical spectrometry, nitriding, steel, wavelength dispersive spectrometer

## 1. Introduction

Nitriding is a well-known thermochemical treatment that is applied to quenched and tempered steels to enhance the fatigue and wear resistance (Ref 1-4). Nitriding is usually carried out in a gas atmosphere consisting of ammonia and hydrogen, at temperatures between 500 and 580 °C. The nitrogen atoms interstitially dissolve in the steel and diffuse away from the surface. The nitriding process develops an affected zone that can be subdivided into a compound layer at the surface and an underlying diffusion layer. In general, the compound layer is formed by nitrides and carbonitrides. The diffusion zone on alloyed steel usually contains interstitially dissolved nitrogen and a fine dispersion of alloying elements (Cr, Mo, Al, and V) nitrides.

The nitrided layers structure depends on the interaction between the diffusional nitrogen and original steel microstructure: ferrite and fine carbides, after quenching and tempering. For example in chromium alloyed steel, the transformation of Cr carbides to Cr nitrides plays a special role, because the conversion of carbides into nitrides occurs more rapidly than the precipitation of the nitrides in the ferrite matrix (Ref 5). The released carbon atoms 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 in the prior steel microstructure. Therefore the nitriding treatment modifies the carbides and C distribution, and this transformation affects also the final hardness profile in the N-enriched layer.

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Occasionally in the industrial practice the work pieces submitted to the nitriding treatment could present some surface decarburization that can be mainly ascribed to the previous quenching and tempering heat treatments. The main differences between the decarburized and the nondecarburized layers are lower carbides content and a larger ferrite grain sizes in the former (Ref 6). The lower carbides content could promote the nitrides direct formation by precipitation from ferrite and not by carbides decomposition. The larger ferrite grain size could induce some modification of the nitrogen diffusion in the affected layer. The aim of this study is to clarify and eventually confirm these effects and to analyze possible differences in the microstructure of nitrided layers deriving from the presence of decarburized layers on the surface. To this end, the behavior of nitrided samples after a controlled surface decarburization has been examined. Moreover, the study could give more information about the effect of preoxidation treatments, often suggested to improve nitrogen take-up during nitriding.

## 2. Experimental Procedure

The study was carried out on the commercial steel UNI-EN 42CrMo4 (composition in Table 1). Various samples, taken from a bar (diameter 28 mm), were heated in air for various times in the temperature range 800 to 900 °C to obtain decarburized layers with a range of depth between 150 and 500 μm. Then the samples were quenched (840 °C, oil) and tempered (600 °C, 2 h). The decarburized layers have been examined by optical microscopy (OM) and the decarburizing thickness was measured following the standard UNI 4839-73.

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

The cross sections of the nitrided specimens were etched with 4% Nital to observe the microstructure and subsequently etched with Murakami to evaluate the distribution of carbides,

**Table 1 Chemical composition of the steel 42CrMo4 (wt.%)**

C	Mo	Mn	Cr	Ni	Cu	Si	Fe
0.432	0.200	0.850	1.148	0.122	0.267	0.243	bal

**Table 2 Decarburized depths**

Sample	0	1	2	3	4	5	6
Decarburized depth, $\mu\text{m}$	0	150	290	300	310	460	490

by light and scanning electron microscopy (SEM). The morphology and distribution of nitrides in the diffusion layers were investigated by SEM in back scattered electron (BSE) mode. Microhardness profiles were performed using a load of 200 g with a Leitz (Wetzlar, Germany) Microindenter. The nitrated surface hardness was measured as  $\text{HV}_{0.2}$ .

The concentration profiles of nitrogen and carbon in the nitride layers have been determined by glow discharge optical spectrometry (GDOS), which operates directly on the surface layers, up to a depth of about 70  $\mu\text{m}$ , with a spatial resolution at nanometer level.

The semiquantitative analysis of carbon and nitrogen in compound and diffusion layers was checked by wavelength-dispersive method (WDS), operating spot by spot on the cross section of the samples, using a Jeol (Tokyo, Japan) JXA-8600 electron microprobe. The Cr, Mo, and Si profiles in the compound layers were obtained with GDS-750A (Leco Corporation, St. Joseph, MI).

### 3. Results and Discussion

#### 3.1 Decarburized Layers

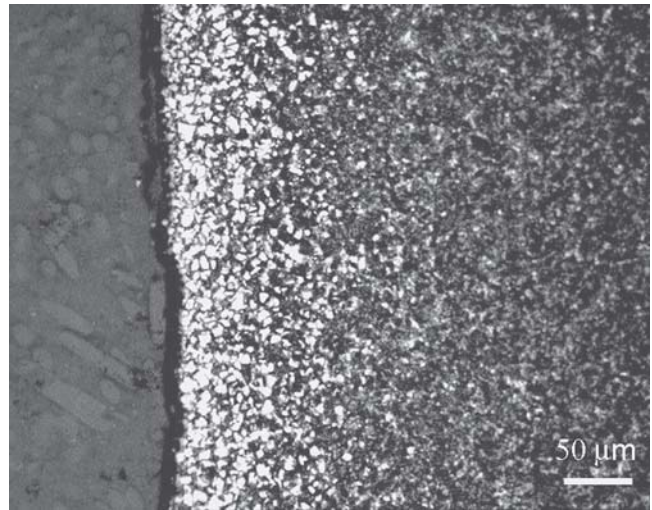
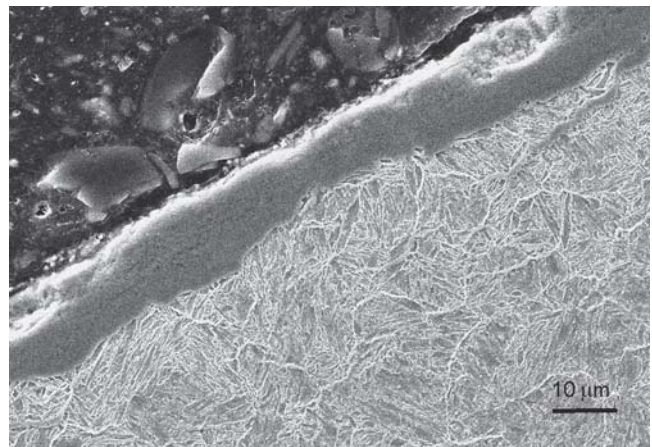
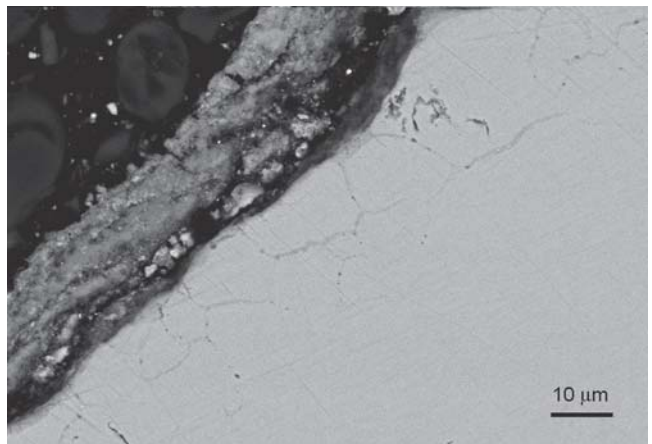
The heat treatment at 800 to 900 °C for 3 to 4 h resulted in decarburized layers of different thickness. Table 2 reports the thickness and the associate sample number; sample 0, not decarburized, was examined for comparison. An example of the decarburized layers microstructure is reported in Fig. 1. The surface layer is completely ferritic with coarse grains and the inner layer, partially decarburized, presents a mixed ferrite-carbides microstructure with some ferrite islands. The amount and dimensions of the ferrite grains decrease gradually to the inner part of the sample, as expected.

#### 3.2 Nitrated Samples

**3.2.1 Microstructure.** Optical and electronic microscopy metallographic investigations were performed to observe the microstructure of the nitrated steel and the influence of decarburization. The results for samples 0 (without decarburizing), 1, and 6, are presented in Fig. 2 and 3.

The micrograph of sample 0 (Fig. 2) shows the typical microstructure of nitriding on a quenched and tempered steel: the outer compound layer and the diffusion zone with nitrides precipitation, more evident at the grain boundaries, are visible. The microstructures of samples 1 (Fig. 4) and 6 (Fig. 5) have the same pattern: the outer compound and the diffusion layer beneath it, but some differences can be observed in both the layers.

The white layer in the decarburized samples is about 30% thinner than in the nondecarburized sample, it appears inhomogeneous, with many voids, widespread porosity, and some cracks.

**Fig. 1** OM of sample 3 (etched with 4% Nital)**Fig. 2** SEM-SE micrograph of sample 0**Fig. 3** SEM-BSE micrograph of sample 6

The outer surface is friable with scaling, mainly in the deeply decarburized samples.

The heterogeneous morphology of the compound layer appears more evident in the SEM-BSE micrographs reported in Fig. 6 (sample 1) and 3 (sample 6), without etching. The

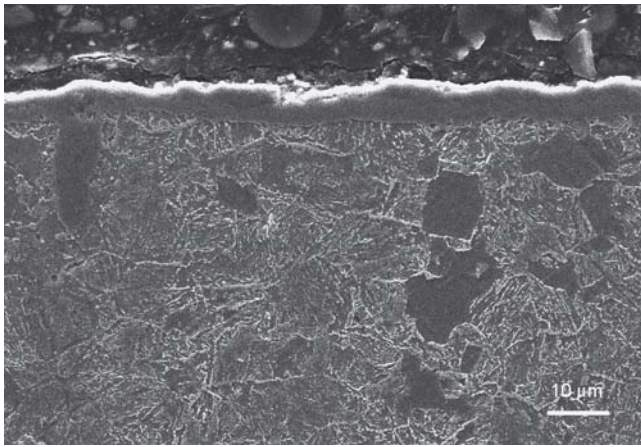


Fig. 4 SEM-SE micrograph of sample 1

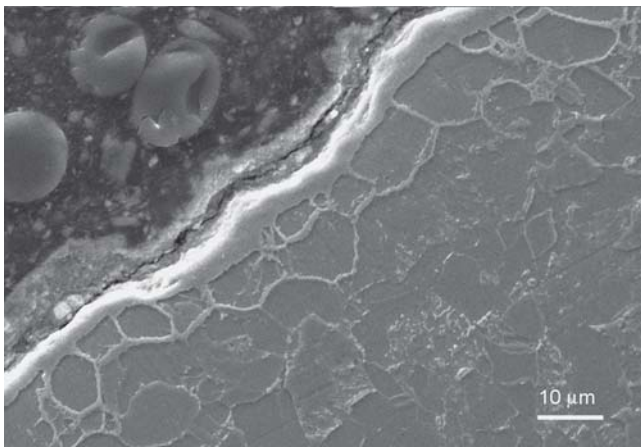


Fig. 5 SEM-SE micrograph of sample 6

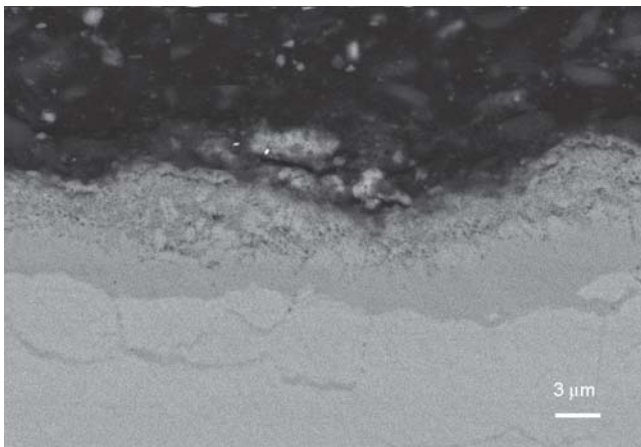


Fig. 6 SEM-BSE micrograph of sample 1

slightly dark outer zone, which corresponds to the compound layer, is irregular and thin, not more than 10 μm, with cracks and widespread porosities, mainly at the surface.

The diffusion zone in sample 1, which is slightly decarburized, has a microstructure quite similar to that of the nondecarburized sample 0. However some ferrite grains remain beneath the compound layer, showing that the previous ferritic

surface layer, produced by the decarburization, has been almost completely replaced by a mixed ferrite/nitrides zone.

On the contrary, in sample 6, which is deeply decarburized, a zone of large ferritic grains, with an evident network of nitrides decorating the grain boundaries, remains beneath the compound layer whereas in the inner zone the nitrides precipitation inside the ferritic grains appears less widespread.

This fact and the evident nitride formation at the grain boundaries of the ferritic zone in the deeply decarburized samples could indicate that the nitrogen diffusion along the grain boundaries is more important than the nitrides formation inside the ferrite grains, by conversion of chromium carbides (no more present in the decarburized layers) is more difficult, or not possible.

**3.2.2 Composition Profile in the Nitrided Layers.** The concentration profiles of carbon and nitrogen on all the thickness of nitriding affected layers were determined by wavelength dispersive electron microprobe analysis (WDS-EPMA). The results, obtained for samples 0, 3, and 6, are given in Fig. 7(a) to (c), along with a comparison of the hardness profiles. The data related to C and N concentrations are expressed as count/s/nA.

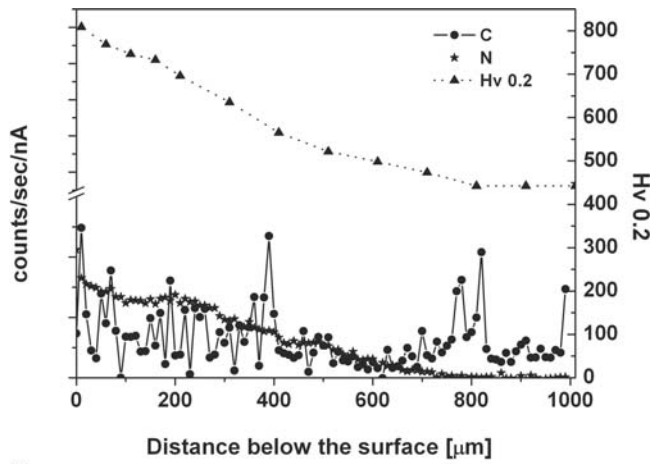
In all the samples the nitrogen content decreases from surface to core, with the mean concentration in the diffusion zones of sample 6 not evidently different, or slightly lower, than in sample 0.

The carbon profiles are obviously more affected by the decarburizing 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 sample 6 show the different depth of the decarburized layer. Some peaks in the profile of sample 3 indicate the presence of a few (small) carbides and the profile of sample 6 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.

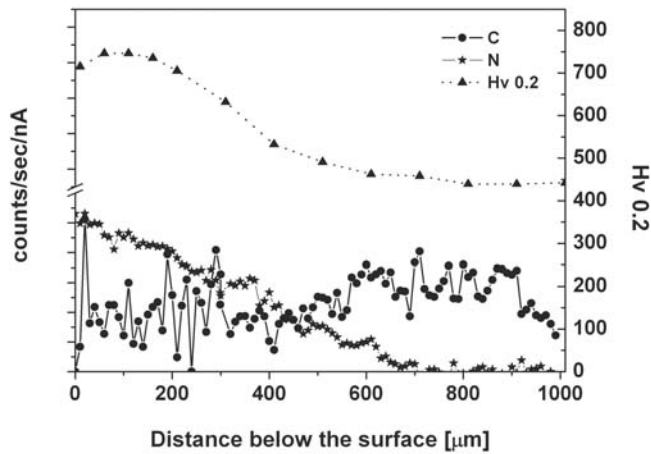
The carbon and nitrogen contents in the compound layers have been examined in more detail using the GDOS. The high initial values of carbon content in the GDOS profiles are due to gas adsorbed on the sample surface and have to be disregarded. The profiles of C and N, obtained on samples 0 and 6, are reported in Fig. 8(a) and (b). The GDOS profile of carbon, in sample 0 after nitriding, shows that carbon appears in the layers at about 10 μm from the surface and its content increases with the depth to reach the base alloy concentration of 0.40%. This carbon loss in the layers near the surface, associated with nitriding is well known (Ref 7): during the nitriding treatment the carbon diffuses to the core as well as to the surface.

In the decarburized samples, the GDOS profiles of C and N show the carbon, as expected, is absent in the analyzed depth (about 70 μm). Instead, in this sample there is an evident higher nitrogen surface concentration (more than 1%), in comparison to that observed in the sample without decarburization, followed by a smooth decrease to a value that remains constant in the examined layer.

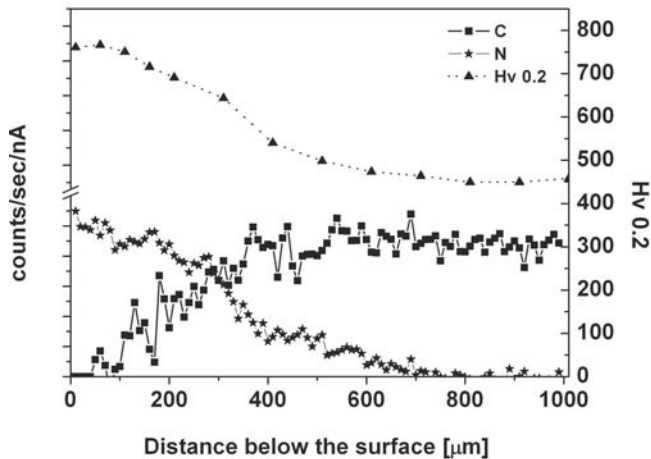
This high nitrogen concentration in the surface layers, both in the compound layer and also beneath it, appears as the main difference, as compared with the nondecarburized sample. The nitrogen content of the compound layer in the sample 0 is about 0.4 wt.%, and reaches a value of 1.5 wt.% in the most decarburized samples. About the same difference remains also in the inner layer, beneath the compound layer. The experimental data suggest that the surface decarburization favors the nitro-



(a)



(b)

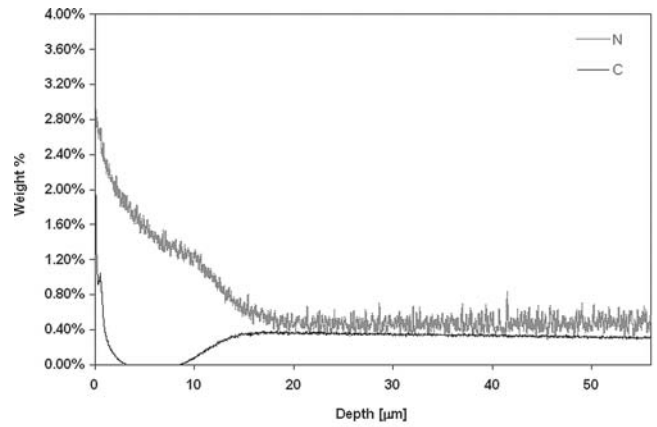


(c)

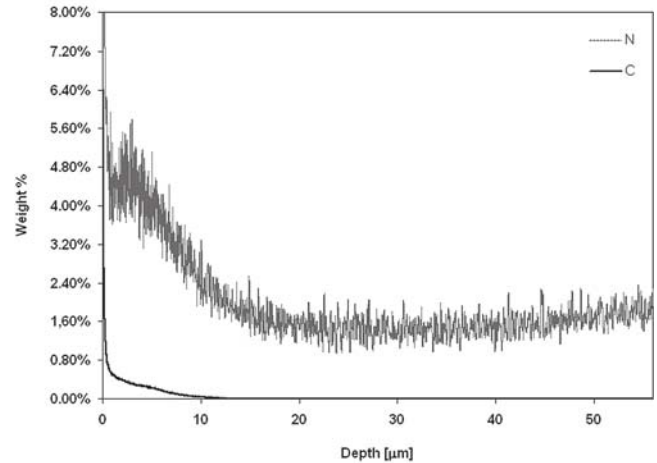
**Fig. 7** (a-c) Nitrogen and carbon EPMA-WDS profiles and hardness profiles of samples 0, 3, and 6

gen take-up and its diffusion, mainly along the grain boundaries and ferrites.

This high nitrogen concentration in the nitriding affected layers of the decarburized samples can justify both the high values of surface hardness after nitriding, despite the lower carbon content of the decarburized layers, and the microstructure of the diffusion zone in the same samples, where, after nitriding, the ferrite grains almost disappear, substituted by a

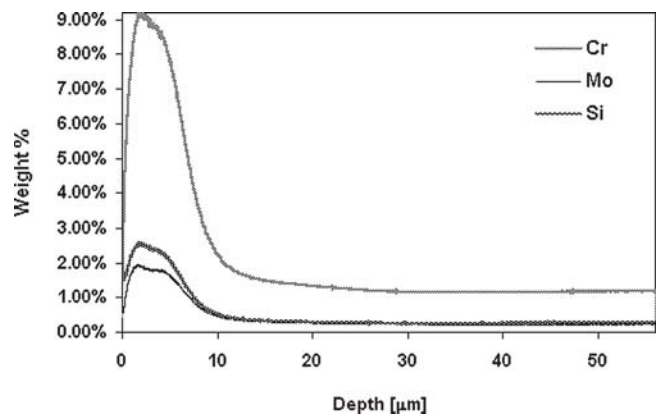


(a)



(b)

**Fig. 8** GDOS profiles of N and C taken on the compound layers of sample (a) 0 and (b) 6



**Fig. 9** GDOS profiles of Mo, Si, Cr on sample 6

fine dispersion of small nitrides formed at the boundaries and inside the ferrite grains.

In the decarburized and nitrided samples, the GDOS measurements give evidence of the surface enrichment in Si, Mo, and Cr, limited to the first 5 to 10  $\mu\text{m}$  of the white layer. The Si and Mo concentrations, measured at the surface, are about 2 wt.%, whereas the Cr concentration reaches 7 to 9 wt.%. It has been verified that a surface enrichment occurs during the

**Table 3 Surface hardness and effective nitrided case depth**

Sample	0	1	2	3	4	5	6
Surface HV <sub>0.2</sub>	841 ± 12	817 ± 10	836 ± 16	810 ± 12	841 ± 12	814 ± 14	817 ± 16
Case depth, μm	480	475	470	445	415	435	390

decarburization heat treatment, before the nitriding. Figure 9 reports the Si, Mo, and Cr profiles in the sample 6, decarburized and not nitrided. The occurrence of Si, Mo, and Cr surface enrichment can be easily explained by their high oxygen affinity, which favors their outward diffusion during the decarburization treatment.

**3.2.3 Hardness.** The surface hardness values and the effective case depth after nitriding are reported in Table 3.

The values of surface hardness are the average of 10 measurements randomly taken on the surface. All the hardness values are higher than the 600 HV required by the standard for the nitrided 42CrMo4 grade. From the data of Table 2, it may be concluded that the surface hardness is not affected by the different rates of decarburization: taking into account experimental errors, the nondecarburized sample 0 has the same hardness as the others.

Also the hardness profiles of all the samples are quite similar, with the typical trend of nitrided steels, showing a decreasing hardness from the surface to the core. The microhardness profiles of samples 5 and 6, superimposed with profiles of sample 0 are reported in Fig. 10. 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 time nitriding process, despite the carbon loss.

The effect of decarburization can be put in evidence by comparing the profiles of samples 1 to 6 with that of sample 0, in the diffusion zone. The hardness values of sample 0 are slightly higher than those of samples 1 to 6; the differences are in the range of 10 to 20 HV and increase as the depth increases. This difference can be explained by the lower hardness values of the base material in the decarburized layers, where only a reduced amount of carbides is present.

However, the consequence of the lower hardness profile is that the effective case depth, after nitriding, decreases. The case depth is generally defined as the depth where the hardness value is 100 HV higher than the core ones. Since the core hardness after tempering in the examined 42CrMo4 steel is 360 HV, the conventional nitriding depth in the case corresponds to 460 HV hardness value. As shown in the Table 3, where the effective depth values are reported, the hardness of 460 HV has been achieved at depths varying from 390 to 480 μm. The value of 480 μm has been measured in the sample 0, whereas the sample 6 (with the deepest decarburization) has the minimum depth of 390 μm.

In all specimens the nitriding depth, determined by the nitrogen profile, is larger than that determined by the hardness profiles. The sensitivity of WDS permits quantitative measurements of nitrogen content with a detection limit of about 0.2%, confirming that low N amounts have a moderate effect on hardness, as suggested in recent papers (Ref 7).

## 4. Discussion

The obtained results are used to analyze the effects of previous decarburizations on nitrided surface layers. Generally the

decarburization cannot reduce the hardness after nitriding, probably because, at the surface, the low carbon content can be compensated by the higher nitrogen enrichment, where the resulting hardness is mainly determined by the nitriding effect.

The main difference between nondecarburized and decarburized samples is, in the former, the high nitrogen concentration in the compound layer and beneath it. The nitrogen content of the compound layer in the sample 0 is about 0.4%, and arrives to the value of 1.5% in the sample 6. The experimental data suggest that the surface decarburization favors the nitrogen take-up during the nitriding treatment. The high nitrogen concentration in the surface layers of the decarburized samples, can justify the high values of the surface hardness after nitriding and the microstructure of the diffusion zone in the same samples. In these areas the ferrite almost disappears and remains only in the deeply decarburized samples, being partially replaced by a mixed zone with a fine dispersion of small nitride particles, formed at the boundaries and inside the ferrite grains.

However in the inner zone, mainly in the diffusion zone of the decarburized samples, the differences in nitrogen enrichment disappear and consequently decrease also the hardness due to the lower carbon content. The consequence is a reduction of the conventional hardened depth produced by nitriding, despite the high surface hardness values.

Finally, the effect of decarburization on the nitrogen take-up and distribution in the nitriding affected layer can be summarized as follows: in the decarburized layer the nitrogen take-up is favored and therefore a high nitrogen concentration and formation of nitrides are produced in the zone (about 100 μm) closer to the surface (the compound layer and a narrow zone beneath it), but the consequence is also a slightly reduced nitrogen concentration and penetration in the inner diffusion zone, as indicated by the WDS results and by the lower hardness profiles.

## 5. Conclusions

The effects of a previous decarburization on properties and structure of nitrided surface layers in a 42Cr4Mo steel can be summarized as follows:

- The surface hardness is slightly affected by a decarburization and the hardness profiles of decarburized samples are a little lower than the profile of the only nitrided sample.
- In all the samples the nitrogen content decreases from the surface to the bulk. In the previously decarburized samples the nitrogen concentration is significantly higher in the first surface layers and slightly lower in the diffusion zones, as compared with the non decarburized sample.
- Consequently in all the specimens the nitriding depth, as determined from the nitrogen profile, is larger than that determined from the hardness profiles, arriving at about 700 μm. Low amounts of interstitially dissolved nitrogen cannot affect the hardness.

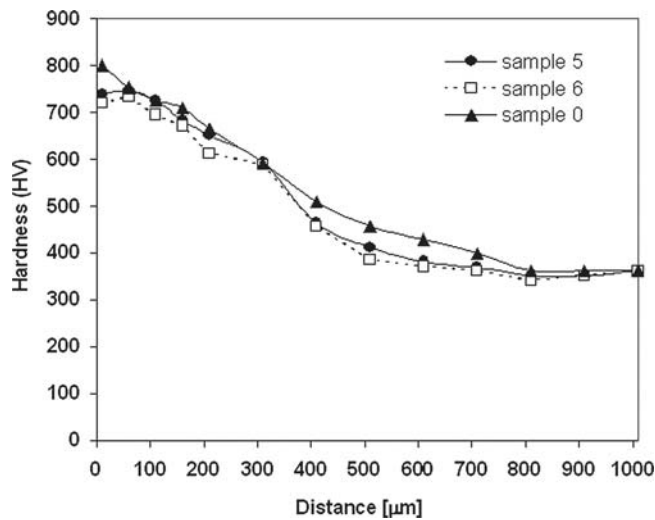


Fig. 10 Hardness profiles of samples 5, 6, and 0

- The main effect of the previous decarburization, on the nitrided layers, seems to be the modification of the nitrogen distribution in the affected layers, with higher nitrogen concentrations in the zone close to the surface.
- It can be concluded that, in industrial applications, a previous surface decarburization does not induce strong det-

rimental effects on the technological properties of nitrided layers, but only a slight decrease of the surface hardness and the conventional nitriding depth. The most harmful effect seems to be the modification of the compound layer that becomes porous and friable.

## References

1. E.J. Mittemeijer and M.A.J. Somers, Thermodynamics, Kinetics and Process Control of Nitriding, *Surf. Eng.*, 1997, **13**, p 483-497
2. R.S.E. Schneider and H. Hiebler, Influence of Increased Nitriding Temperatures on the Hardness Profile of Low-Alloy Steel, *J. Mater. Sci.*, 1998, **33**, p 1737-1744
3. J. Ratajski, J. Tacikowski, and M.A.J. Somers, Development of Compound Layer of Iron (Carbo)Nitrides during Nitriding of Steel, *Surf. Eng.*, 2003, **19**, p 285-291
4. P. Egert, A.M. Maliska, H.R.T. Silva, and C.V. Speller, Decarburization during Plasma Nitriding, *Surf. Coat. Technol.*, 1999, **221**, p 33-38
5. P.C. Van Wiggeren, H.C.F. Rozendaal, and E.J. Mittemeijer, The Nitriding Behaviour of Iron-Chromium-Carbon Alloys, *J. Mater. Sci.*, 1985, **20**, p 4561-4582
6. P. Filippi and G. Rossetti, Indagine Strutturale Degli Strati Nitridati in Funzione della Decarburazione per l'acciaio Uni 38CrAlMo7 (Microstructural Characterization of a Decarburized and Nitrided Uni 38CrAlMo7 Steel) *Met. Ital.*, 1975, **67**(10), p 605-609, in Italian
7. B.M. Korevaar, S. Coorens, Y. Fu, J. Sietsma, and S. van der Zwaag, Effects of Nitriding on Fatigue Strength of Quenched and Tempered Steel: Role of Interstitial Nitrogen, *Mater. Sci. Technol.*, 2001, **7**, p 54-62