COURRIER DU SAVOIR – N°05, Juin 2004, pp.63-68

FORMATION OF LAYERS BY PLASMA NITRIDING IMPOSED TO 32CrMoV13 LOW ALLOY STEEL

FORMATION DES COUCHES PAR NITRURATION PLASMA IMPOSEE A L'ACIER FAIBLEMENT ALLIE 32CrMoV13

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ABSTRACT

The aim of the study is to optimise the application of heat treatments by modifying the nitriding conditions in high temperature process. The influence of gas mixture (composed of N_2, H_2 and CH_4) and time of nitriding on the mechanical and structural properties of 32CrMoV13 low alloy steel samples was studied. The composition and structure of the nitrided layers was determined by EDS and XRD respectively. Vickers micro hardness profiles were also performed to study the influence of the gas mixture and time of nitriding. The morphology of the nitrided layers was observed by optical microscopy. EDS analyses permitted to verify the composition of the layers while their structure was determined by XRD.

The time of nitriding was influent on the diffusion layer's thickness and properties. Furthermore, it was obvious that increasing the nitrogen contents from 20 to 80 % in the nitriding gas mixture N_2+H_2 or adding 5% of methane permits to increase the nitrided layer's thickness and hardness. The duplex treated samples obtained with 80 % of N_2 or 5% CH_4 performed best and allowed to increase almost twice the tools service life.

KEYWORDS: Plasma nitriding, gas mixture, low alloy steel, nitriding layers.

RÉSUMÉ

Le but de ce papier est d'optimiser le traitement thermique de nitruration ionique par plasma et ce en modifiant les conditions de nitruration à haute température. L'influence du mélange gazeux (composé de N_2, H_2 et CH_4) et le temps de nitruration sur les propriétés mécaniques et structurales de l'acier faiblement allié 32CrMoV13 a été étudié. La composition et la structure des couches de nitruration ont été déterminées par microanalyse EDS et diffraction des rayons X respectivement.

Des profiles de microdureté Vickers ont été réalisés afin de voir l'effet du mélange gazeux et du temps de nitruration. La morphologie des couches a été observée par microscopie optique.

Le temps de nitruration influe directement sur l'épaisseur et les propriétés des couches blanches et de diffusion. Il est évident que l'augmentation du pourcentage d'azote de 20 à 80 % dans le mélange gazeux (N_2+H_2) ou l'addition de 5 % de méthane (CH_4) conduit à une augmentation remarquable de la dureté et des épaisseurs des couches.

MOTS CLES : Nitruration plasma, mélange gazeux, acier faiblement allié, couches nitrurées

ملخص

الهدف من هذه الدراسة هو البحث عن المعالجة الحرارية المثلى في عملية النتردة الأيونية بواسطة البلازما و ذلك بتغيير الشروط عند درجة حرارة عالية.

تمت دراسة تأثير المزيج الغازي (المكون من النتروجين، الهيدروجين و الميثان) و كذا زمن عملية المعالجة بالنتردة على الخصائص الميكانيكية و البنيوية للفولاذ منخفض السبيكية 32CrMoV13**. تم تحديدي تركيب و بنية الطبقات المتكونة إثر عملية النتردة بواسطة التحليل الطيفي** EDS **و الأشعة السينية** DRX **على التوالي.**

سمحت منحنيات تغيرات الصلادة بواسطة المزيج الغازي و زمن النتردة بدراسة تأثير هذه الوسائط على تكون الطبقات كما سمح المجهر الضوئي بمتابعة البنى المجهرية.

لوحظ أن زمن النتردة له تأثير مباشر على السمك و على خصائص الطبقات البيضاء و طبقات الانتشار. كما وجد أن زيادة نسبة الأزوت في المزيج (N_2+H_2) من 20 إلى 80 بالمائة أو إضافة 5 بالمائة من غاز الميثان تؤدي إلى زيادة معتبرة في سمك و صلادة الطبقات المتكونة.

كلمات مفاتيح : نتردة أيونية، مزيج غازي، فولاذ منخفض السبيكية، طبقات نتردة.

1 INTRODUCTION

Actually, hard coatings are commonly used to increase the wear resistance of cutting tools in metal machining [1]. In wood machining, even if the application of coatings as wear or corrosion protection of cutting knives is not common, some previous works [2] showed their efficiency in peeling and routing. Even if the coatings allowed increasing the service life of the cutting tools, their adhesion is not sufficient. This could be a limit to their employment and marketing. Nevertheless, the solution to increase the adhesion of the coatings on steel tools was to realise a previous nitriding to the tool before the coating: that means to make a duplex treatment. Previous works showed the efficiency of TiN-based [3,4], Cr_2N-based [5] and TiN/TiAlN-based [6] duplex treatments. Smolik et al. [7] particularly showed that CrN-based duplex treatments performed the best compared to TiN-based ones in wear tests with a Z155CrMoV131 steel ball. A preliminary study was realised on steel 60SMD8, unsuitable for nitriding, but commonly used in peeling of beech [2]. During the peeling of beech, the CrN-based duplex treatments permitted to increase 4 times the service life of cutting knives while the CrN-coated ones permitted to increase the service life only 1,3 times. The aim of this work is to complete the study of the application of CrN-based duplex treatments by determining the influence of nitriding parameters, such as the gas mixture, and especially methane, and the time of treatment on the mechanical and structural properties of nitrided steel samples and knives. The steel material was 32CrMoV13 low alloy steel, of composition: C 0.3, Si 0.31, Mn 0.5, Cr 3.25, Mo 0.44, Ni 0.11, V 0.1, commonly used for nitriding and presenting a good tenacity.

2 EXPERIMENTAL DETAILS

Nitriding treatments have been carried inside a low vacuum furnace (450x450x450 mm^3) equipped with an impulsive current generator. The temperature of the samples is followed thanks to a thermocouple very close to them. The type of nitriding layers and their qualities depend on the type of gas mixture, the pressure and time of nitriding process [3, 8]. The applied nitriding conditions are summarized in Table 1. The cutting material 32CrMoV13 was chosen because it presents a good amount of Cr, Mo and V necessary for a good nitriding. The treated cutting tools were tested in peeling of beech.

Table 1 : Nitriding conditions applied on 32CrMoV13 steel at 510°C.

	Gas mixture	Time of nitriding (hours)
A	20% N_2 + 80% H_2	2, 4, 6, 8
B	20% N_2 + 75% H_2 + 5% CH_4	2, 4, 6, 8
C	75% N_2 + 20% H_2 + 5% CH_4	2, 4, 6, 8
D	80% N_2 + 20% H_2	8

The thickness and morphology of nitrided layers were observed by optical microscopy on cross sections (OLYMPUS VANOX-T AH-2 microscope). The composition of the nitriding layers was verified by EDS (Energy Dispersive Spectroscopy) analyses and X-Ray Diffraction analyses (SIEMENS D500 - K_α (Co) radiations) were performed to determine their structure.

XRD analyses were also used to determine the residual stresses of these layers (Diffractometer Siemens D500 - K_α (Cr) radiations) [9]. The stress profiles were obtained after erosion of 10 to 60 μm in anodic dissolution with an appropriate electrolyte. The used peak was the Fe (211) and the radiocristallographic constant ½ S_2 (211) was taken to the one of Fe : 0,585 10^{-5} MPa^{-1}. Vickers hardness measurements (microdurometer LECO AMH 100 - load 200 g) have been also performed on steel samples.

3 RESULTS AND DISCUSSION

The presence of nitrogen was verified by EDS analyses which reveal a peak at 392 eV characteristic of N ($K_{\alpha 1}$). For all gas mixtures, we found that this peak increases with time (Fig. 1A, B, C, D).

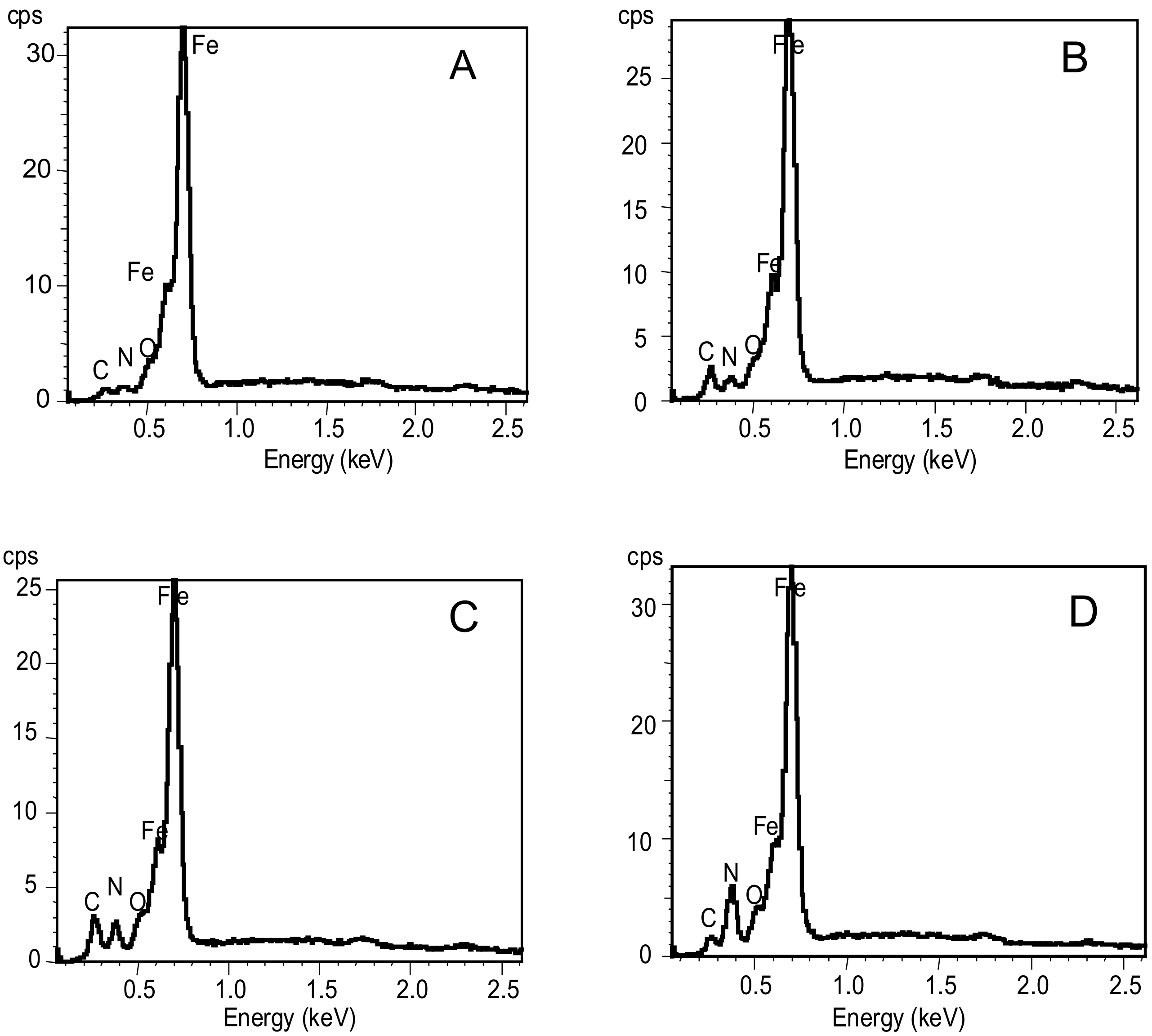

Fig.1 : EDS spectra corresponding to 75%N$_2$+20%H$_2$+5%CH$_4$ gas mixture ((A) 2, (B) 4, (C) 6 and (D) 8 hours).

Optical observations of the nitrided layers reveal the presence of a thin white layer (2-20µm) and a diffusion layer obtained in B, C and D gas mixture for all times. However, we don't found a white layer in A gas mixture whatever the nitriding time (Fig.2A). This layer was observed in the other gas mixture after only 2 hours of nitriding time (Fig.2B,C,D).

The presence of a dense white layer was verified by XRD analyses (Fig. 3). Composed of two phases γ'(Fe$_4$N) et ε(Fe$_{2\text{-}3}$N), this layer is present in B, C and D samples. It appears that the thickness of the γ' phase decreases when the nitrogen contents of the nitriding gas mixture increases or when methane is present. Confente et al. [10] showed that in both cases, it tends to generate or stabilise the ε phase in the nitrided layer. In this case, we observe an increase of the well crystallised ε diffusion layer's thickness on the XRD patterns.

It also appears that the thickness of the diffusion layer is thinner in the case of the mixture A, where the Fe (200) and (211) peaks are still well detected in comparison to the other mixtures, where only broad Fe (211) and (110) peaks are observed. Furthermore, for 20% of nitrogen in the nitriding gas mixture, only the ε (002), ε (110) and ε (112) peaks are detected. When the nitrogen contents increases to 80%, ε (100), ε (211), ε (101), ε (121), ε (102) and ε (103) peaks are also detected. The influence of methane decreases due to the saturation of nitrogen concentration.

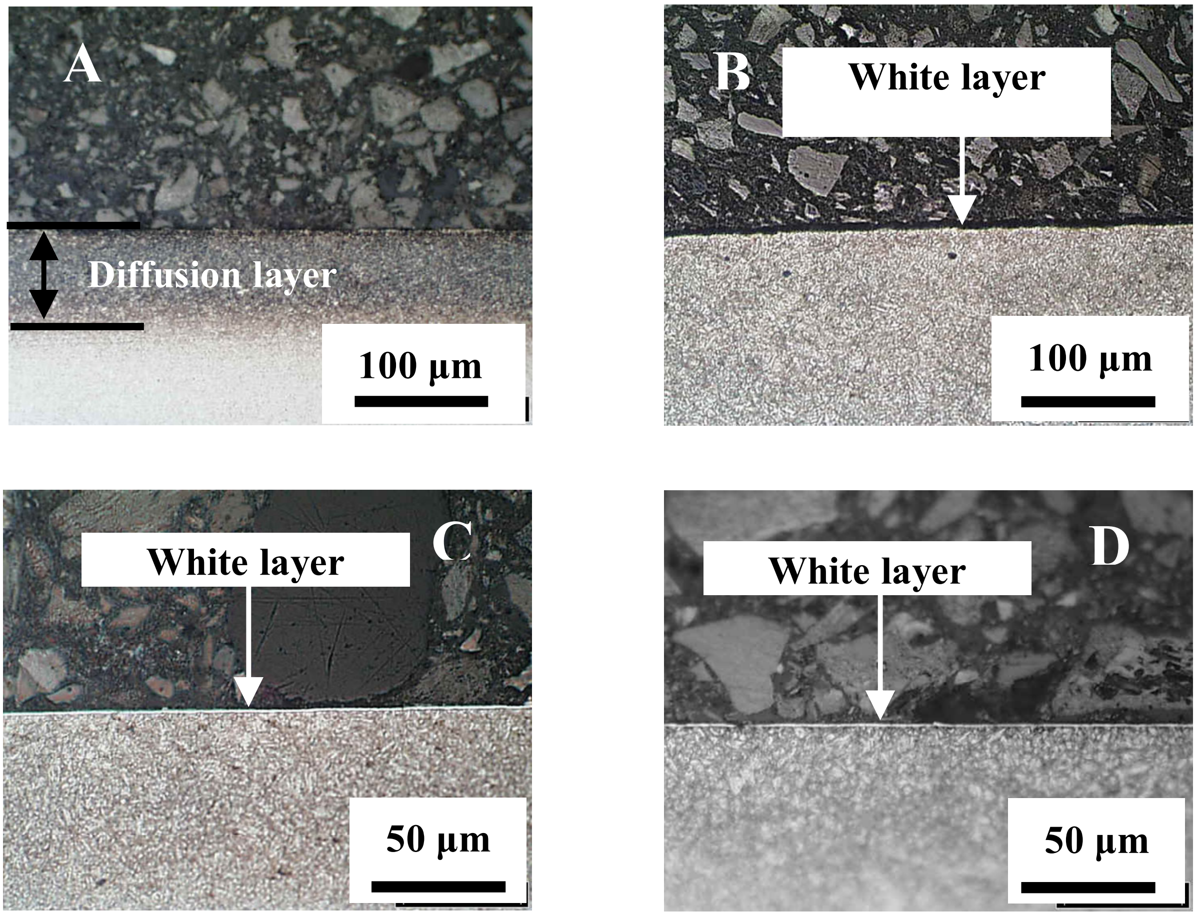

Fig.2 : *Cross-section observations of steel samples nitrided in: (A) 8 hours in gas mixture A, (B) 2 hours in gas mixture B, (C) 2 hours in gas mixture C, (D) 2 hours in gas mixture D.*

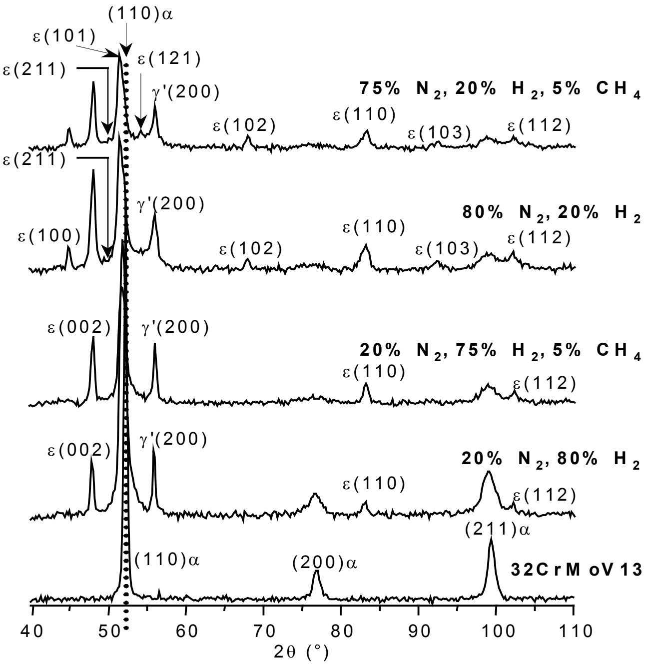

Fig.3 : *XRD patterns as a function of the nitriding gas mixture after 8 hours of nitriding.*

The hardness profiles of untreated and nitrided steel samples are represented in figure 5. the steel sample nitrided in a gas mixture A has a higher surface hardness (850 HV) than the untreated one (500 HV) but lower than the three other nitrided steel samples B, C and D which present a surface hardness of around 900 – 1000 HV.

The increase of nitrogen contents from 20 to 80% or the introduction of methane in the gas mixture permit to reach a higher surface hardness. The hardness profiles permit also to verify the nitrided layer's thickness as a function of nitriding gas mixture (Fig.4A) and time of nitriding (Fig.4B). The gas mixture A allowed to get a nitrided layer of 100 µm while other gas mixture with higher N_2 contents or 5% CH_4 allowed to reach a thickness around 200 µm. These results confirm the ones obtained by optical observations (Fig. 3). Furthermore, as expected, the thickness of the nitrided layers increases with the time of nitriding (Fig.5B).

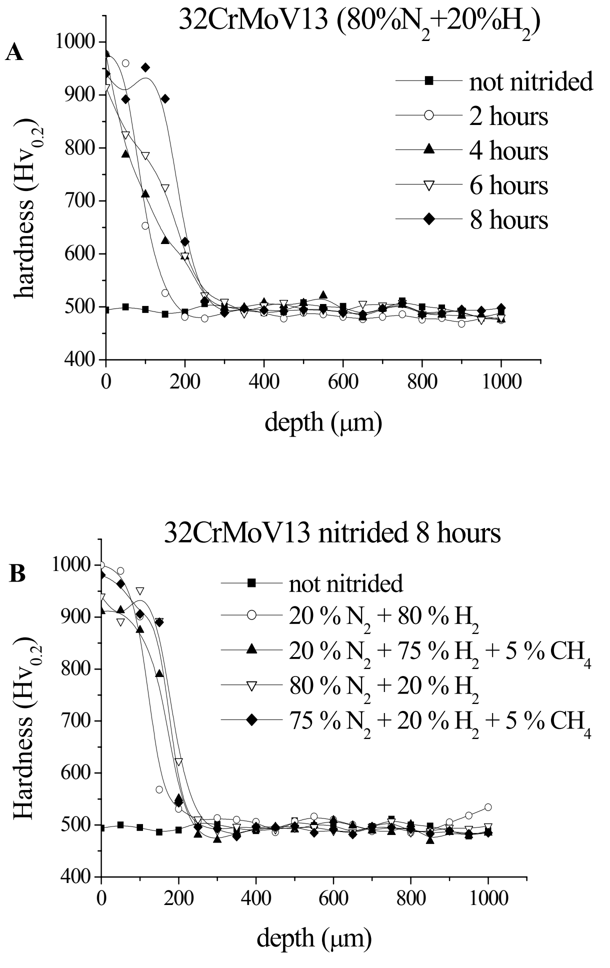

Fig.4 : *Vickers hardness profiles as a function of gas mixture (A) and nitriding time (B).*

X-Ray measurements present that the nitrided layers have compressive stresses [11] with a maximum of –800 MPa at the depth of 80 µm (middle of the nitrided layer thickness) (Fig.5). The stress must be homogenous in the nitrided layer because it doesn't depend on the Φ direction (direction of analyses).

Correlation between the stress and the hardness is shown on the figure 6B but due to surface effect, it was not possible to measure the hardness under 25 µm of depth. We can observe two zones: zone I where the creation of interstitial nitrogen (iron nitrides) and the nitrides precipitation into the matrix is main close to the surface. This is responsible for the increase of hardness and stress simultaneously. In zone II, the stress tends to stabilize or slowly decrease because of a possible relaxation [11]. Previous works showed such correlation for 32CrMoV13 steel samples gas nitrided at 550°C [12].

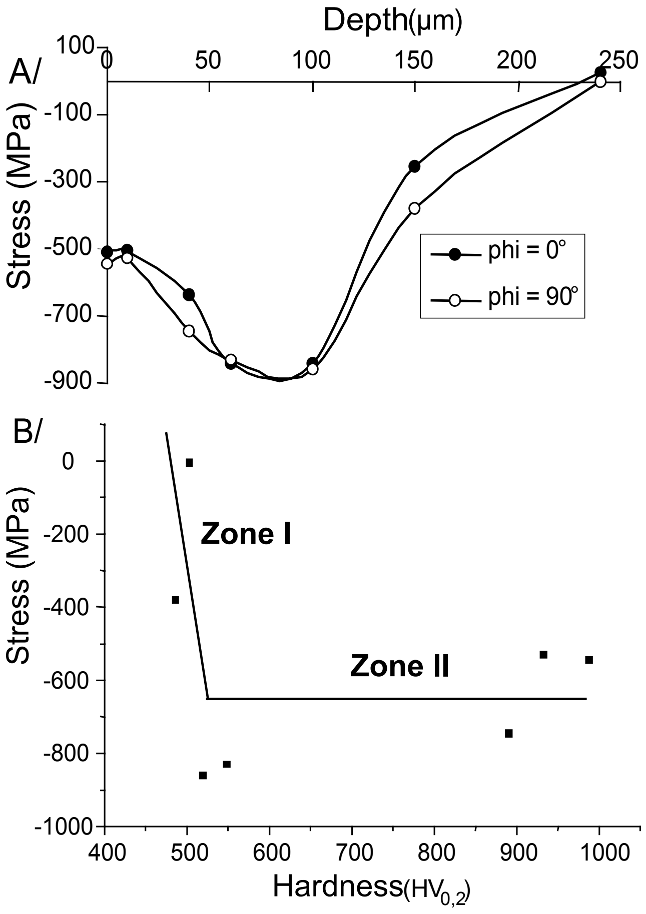

Fig.5 : *Stress profiles versus depth (A) - Relation between stress and hardness for a steel sample nitrided with 80%N_2+20%H_2 (B)*

4 CONCLUSION

The influence of nitriding gas mixture and time on the properties of 32CrMoV13 nitrided samples was studied. It was shown that increasing the nitrogen contents from 20 to 80% or time of nitriding from 2 to 8 hours or adding 5% of methane in the nitriding gas mixture permit to increase the hardness and the thickness of the nitrided layer. It appears that nitrocarburizing is as efficient as the nitriding process and could be economically more interesting. Indeed, adding only 5% of methane in a nitriding gas mixture composed of only 20% of nitrogen allows to obtain a nitrided layer with equal mechanical properties than the one obtained with 80%N_2+20%H_2.

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