Determination of the Optimum Conditions for Ion Nitriding of 32CDV13 Low Alloy Steel

Chahinez Saied, Abdelouahad Chala,* Corinne Nouveau, Mohamed Abdou Djouadi, Lounis Chekour

The excellent mechanical properties of chrome-vanadium low alloy steel usually obviate the need for expensive quench and tempering operations. Furthermore, the presence of a significant amount of nitride phases has generated interest in the applicability of this kind of steel to fabricate tools with good corrosion and wear resistance. In this paper, 32CDV13 low alloy steel was ion nitrided under different process parameters including time (2, 4, 6 and 8 h), temperature (380, 500 and 580 °C) and gas mixture (N_2, H_2 and CH_4). By determining phase composition, hardness profiles, compound layer thickness and case depth, the optimum working conditions were determined. Microhardness tester, X-ray diffraction and scanning electron microscopy were utilised to characterise the nitrided surfaces. The observed differences in the hardness, the thickness and the structure of the compound layers and the diffusion zones are discussed. The optimum results were obtained at $75\%N_2 + 20\%H_2 + 5\%CH_4$ gas mixture, at the temperature of 500 °C and for a process time of 8 h.

Introduction

Ion nitriding has found increasing applications in the industry owing to a number of advantages over the conventional nitriding process.

Different structures can occur at the surface of the steel as a result of ion nitriding. This surface layer is commonly known as the white layer or compound layer and it is formed by the ε-$Fe_{2\text{-}3}N$ phase and/or γ'-Fe_4N. The microstructure of the compound layer can be affected by process parameters such as temperature, gas mixture composition and time. The change of the microstructure of the surface layer affects mechanical properties of materials.

Actually, hard coatings are commonly used to increase the wear and corrosion resistance of cutting tools in metal machining.[1] 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.[2] Although controversies exist in the literature to know which nitride layer is useful for industrial applications, it is generally accepted that heterogeneous biphased compound layers must be avoided because they tend to spall.[3–5]

Improved adhesion behaviour is expected when the coating is directly deposited onto an α-Fe diffusion layer

C. Saied, A. Chala*
Laboratoire de Chimie Appliquée, Université de Biskra, BP 145 RP, 07000 Biskra, Algérie
Fax: (+213) 33 74 61 62; E-mail: ab_chala@yahoo.fr
C. Nouveau
Ecole Nationale Supérieure d'Arts et Métiers, La.Bo.Ma.P. 71250 Cluny, France
Md. A. Djouadi
Institut des Matériaux Jean Rouxel, Laboratoire des Plasmas et des Couches Minces, 44000 Nantes, France
L. Chekour
Laboratoire des Couches Minces et Interfaces, Université Mentouri, 25000 Constantine, Algérie

Element	C	Cr	Mo	V	Ni	Mn	Si
Wt.-%	0.32	3.25	0.44	0.013	0.11	0.52	0.31

or after removal of the compound layer (called white layer) by polishing.[6,7] As a result, the optimisation of ion nitriding conditions requires a good control of the nitriding parameters, especially temperature, time of nitriding and gas mixture composition to produce a suitable nitrided case.[8]

The aim of this work is to study the nitriding treatments' process by determining the influence of different parameters, such as the temperature, the gasmixture, especially methane, and the time of treatment on the mechanical and structural properties of nitrided steel samples and knives.

Table 2. Nitriding conditions.

	Gas mixture	Temperature	Time of nitriding
		°C	h
A	$20\%N_2 + 80\%H_2$	380, 500, 580	2, 4, 6, 8
B	$20\%N_2 + 75\%H_2 + 5\%CH_4$	380, 500, 580	2, 4, 6, 8
C	$75\%N_2 + 20\%H_2 + 5\%CH_4$	380, 500, 580	2, 4, 6, 8
D	$80\%N_2 + 20\%H_2$	380, 500, 580	2, 4, 6, 8

Experimental Part

Nitriding treatments have been carried inside a low vacuum furnace ($450 \times 450 \times 450$ mm^3) equipped with an impulsive current generator. The temperature of the samples is followed thanks to a thermocouple very close to them.

The material used in this study was 32CDV13 low alloy steel; its chemical composition (wt.-%) is given in Table 1. This material is commonly used for nitriding and presenting a good tenacity and can provide a higher core strength and a more gradual hardness gradient from the surface layer down to the core. This cutting material was also, chosen because it presents a good amount of Cr, Mo and V necessary for a good nitriding.

The type of nitriding layers and their qualities depend on the type of gas mixture, the pressure and time of nitriding process.[3,7–11] The applied nitriding conditions are summarised in Table 2.

Before nitriding, a previous pretreatment of samples is necessary to ensure appropriate mechanical characteristics at the surface and compatibility the core for all future use. In our case, the cycle of the pretreatment was: heating at 600 °C for 15 min, heating at 800 °C for 15 min, heating at 900 °C immediately followed by quenching in nitrogen environment (5 bar), annealing at 550 °C for 1 h and finally, a very slight quenching in nitrogen (1 bar). The microhardness of samples after this treatment was found approximately 500 HV.

The thickness and the morphology of nitrided layers were observed by a Olympus Vanox AH-2 optical microscope and Jeol 5900 scanning electron microscope (SEM). The composition of the nitriding layers was verified by energy dispersive spectroscopy (EDS) analyses, and X-ray diffraction (XRD) analyses with CoKα radiations were performed to determine their structure. Vickers microhardness measurements (LECO AMH 100, load 200 g) have been performed on steel samples.
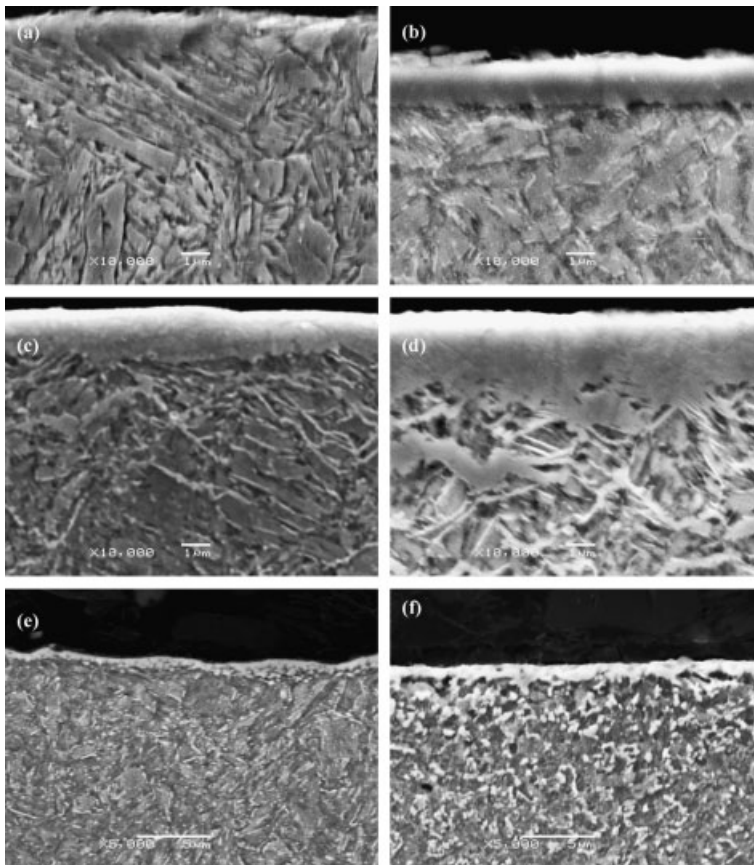

Figure 1. SEM images of cross-sections of 32CDV13 samples nitrided 8 h under different conditions: (a) $20\%N_2 + 80\%H_2$, 500 °C; (b) $40\%N_2 + 60\%H_2$, 500 °C; (c) $60\%N_2 + 40\%H_2$, 500 °C; (d) $80\%N_2 + 20\%H_2$, 500 °C; (e) $80\%N_2 + 20\%H_2$, 380 °C; (f) $80\%N_2 + 20\%H_2$, 580 °C.

Results and Discussion

Samples of 32CDV13 were treated for a process time of 8 h at temperatures T between 380 and

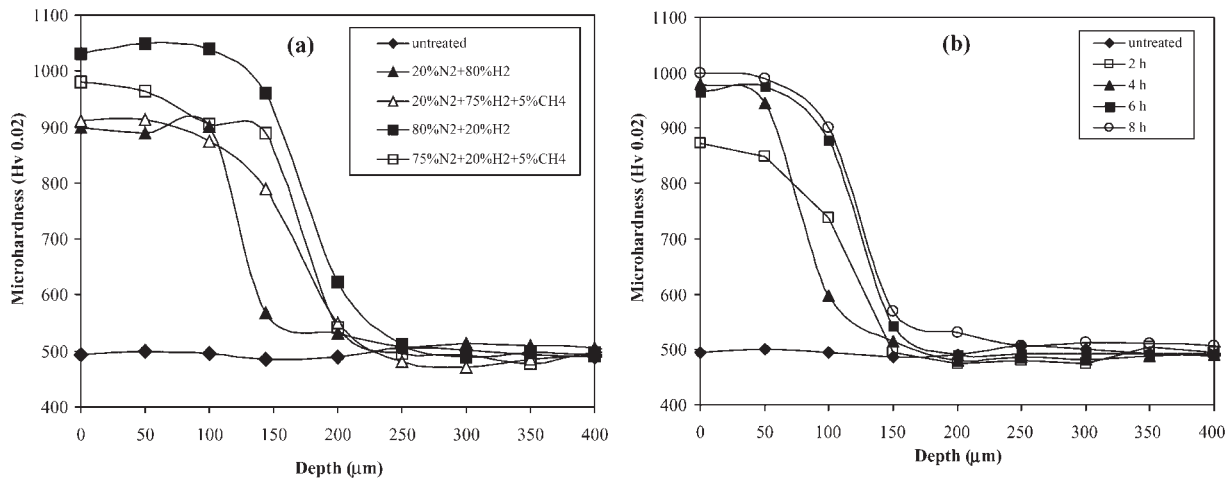**Figure 2.** Variation of microhardness as a function of depth: (a) $T = 500\,°C$, $t = 8$ h, different gas mixture; (b) $T = 500\,°C$, $80\%N_2 + 20\%H_2$, $t = 2$–8 h.

580 °C in different gas mixtures. The influence of temperature and gas mixture ratio on the microstructure can be seen in the cross-sectional SEM micrographs [Figure 1(a–f)].

A thin white layer and a diffusion layer are observed for all the samples expect for Figure 1(a) obtained with 80% H_2 in the gas mixture. The compound layer is absent here due to the less percentage of nitrogen. The decrease in H_2 from 80 to 20% is responsible for the increase in the compound layer's thickness from 1 to 3 μm [Figure 1(b–d)]. A compound zone with a nonuniform thickness of 3–5 μm is revealed when 80% N_2 is used in the gas mixture [Figure 1(d)].

The influence of temperature is clearly seen in Figure 1(e–f). The increase in the temperature from 380 to 580 °C favours denitriding and decarburising of the diffusion layer and as result the compound layer becomes very heterogeneous and may contain nitrides like CrN or VN which decrease the mechanical properties of the steel.

The effect of gas mixture composition and time on the microhardness depth profiles in the nitrided samples is presented in Figure 2. The temperature remains constant ($T = 500\,°C$). It is clear that the microhardness is sensible to the gas mixture and time of nitriding. Figure 2(a) shows the variation of microhardness with depth for four gas

mixtures. The presence of 20% of H_2 gives the highest surface microhardness and the layer thickness is the most important in this case. Excessive amounts of hydrogen retard the nitriding process.[12–14] The addition of only 5% CH_4 in the gas mixture can also be useful to obtain good surface hardness and results in thicker layers. Increasing time nitriding influences directly the surface hardness which can reach 900 HV after 4 h of nitriding and exceed 1 000 HV after 8 h of nitriding [Figure 2(b)].

The XRD analysis presented in Figure 3 shows results of nitrided 32CDV13 low alloy steel as a function of gas mixture ratio (N_2/H_2). In these tests we fixed $T = 500\,°C$ and
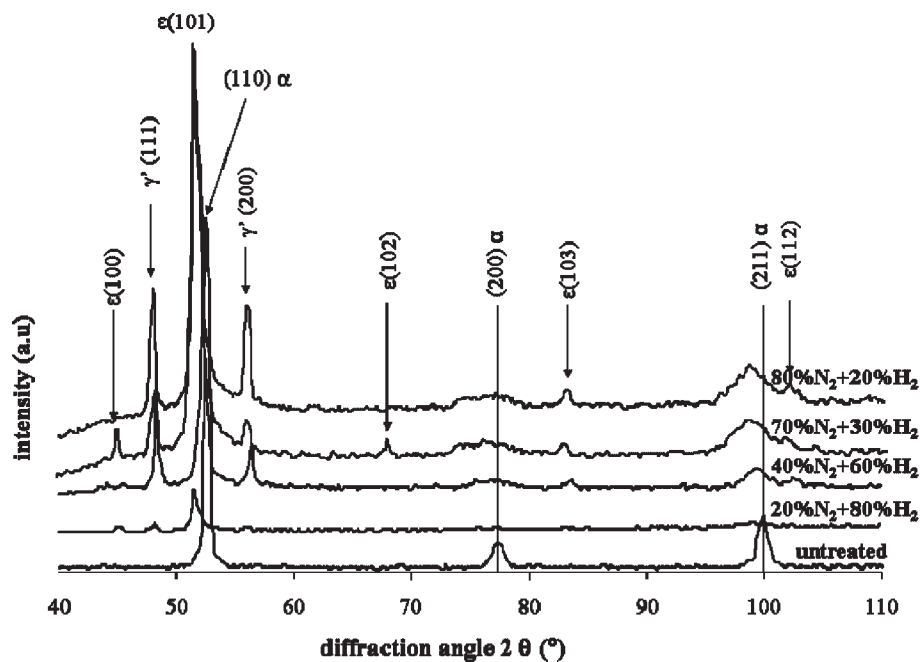

Figure 3. X-Ray diffraction patterns as a function of gas mixture.

$t = 8$ h. As seen in the figure, polyphase (γ' and ε) iron nitride was produced on the surface of the low alloy steel. With increasing gas mixture ratio, the intensity of the ϵ nitride phase decreases whereas the intensity of γ' nitride phase increases. A careful examination of the figure shows that the intensity of ε nitride decreases when the gas mixture ratio reaches 2.3. The gradual decrease in the amount of the ε nitride phase could be caused by denitriding, decarburisation or decrease in the carbon content of steel due to sputtering.[15]

Conclusion

The optimum conditions of 32CDV13 low alloy steel nitriding were determined in this work. It was found that in a poor atmosphere of nitrogen, there is only formation of diffusion layer on the surface of steel. The addition of a little quantity of methane can produce a thinner compound layer which increases with increasing nitrogen concentration. This can also lead to increase spectacularly the thickness of the diffusion layer ($\times 2$) and the surface microhardness higher than 900 HV. The mechanical properties are very interesting when the compound layer is formed essentially by only one phase (γ' or ϵ). The presence of the polyphase layer tends to form high stresses at the surface and provoke hard fissures unsuitable for industrial applications.

The most important parameter on the surface hardness is found to be the temperature. The maximum was obtained at 500 °C, 80%N_2 + 20%H_2 gas mixture for 8 h time.

The time of nitriding is the most effective parameter on the depth. The maximum case depth was observed for the maximum time nitriding.

The optimum conditions are reproducible in laboratory but it is difficult to say the same thing in real production environments. However, we think that this study may be very useful for ion nitriding process in industrial scale.

[1] M. V. Stappen, M. Kerkhofs, L. M. Stals, C. Queyhaegens, *Surf. Coat. Technol.* **1995**, *74–75*, 629.
[2] C. Nouveau, M. A. Djouadi, R. Marchal, M. Lambertin, *Méca Indus.* **2002**, *3*, 333.
[3] A. Alsaran, A. Çelik, C. Çelik, *Surf. Coat. Technol.* **2002**, *160*, 219.
[4] S. K. Kim, J. S. Yoo, J. M. Priest, M. P. Fewell, *Surf. Coat. Technol.* **2003**, *163–164*, 380.
[5] E. J. Miola, S. D. De Souza, M. Olzon-Dionysio, *Surf. Coat. Technol.* **2003**, *167*, 33.
[6] L. Chekour, C. Nouveau, A. Chala, M. A. Djouadi, *Wear* **2003**, *255*, 1438.
[7] J. Musil, J. Vlček, M. Růžička, *Vacuum* **2000**, *59*, 940.
[8] A. Alsaran, A. Çelik, *Mater. Charact.* **2001**, *47*, 207.
[9] A. Chala, L. Chekour, C. Nouveau, C. Saied, M. S. Aida, M. A. Djouadi, *Surf. Coat. Technol.* **2005**, *200*, 512.
[10] A. M. Abd El-Rahman, F. M. El-Hossary, T. Fitz, N. Z. Negm, F. Prokert, M. T. Pham, E. Richter, W. Möller, *Surf. Coat. Technol.* **2004**, *183*, 268.
[11] F. S. Chen, C. N. Chang, *Surf. Coat. Technol.* **2003**, *173*, 9.
[12] J. Barralis, J. C. Chaize, *Traitement Thermique* **1985**, *197*, 59.
[13] B. Larisch, U. Brusky, H. J. Spies, *Surf. Coat. Technol.* **1999**, *116–119*, 205.
[14] M. P. Fewell, J. M. Priest, M. J. Baldwin, G. A. Collins, K. T. Short, *Surf. Coat. Technol.* **2000**, *131*, 284.
[15] A. Chala, C. Nouveau, M. A. Djouadi, P. Steyer, J. P. Millet, C. Saied, M. S. Aida, M. Lambertin, *Surf. Coat. Technol.* **2006**, *200*, 6568.