

# ENHANCEMENT OF THE MECHANICAL PROPERTIES OF GRAYCAST IRON BY FERRITIC NITROCARBURIZING PROCESS

Samira TLILI\*, Mohamed Zine TOUHAMI\*\*

\*Unité de Recherche Appliquée en Sidérurgie Métallurgie URASM/ CSC BP 196 23 000  
Annaba, Algérie.

\*\*University of Annaba, Department of Metallurgy-  
Laboratory of Foundry –UBM-Annaba-Algeria [tlili\\_s@yahoo.fr](mailto:tlili_s@yahoo.fr)

## ABSTRACT

*In this paper, we studied the mechanical properties of green cast iron ferritic nitrocarburizing after treatment in salt bath at 580°C at different holding time. The nitrocarburizing process has contributed changes in surface properties.*

*After characterization and analysis the microstructure by scanning electronic microscopy and X-ray diffraction, the obtained results show that the structure led to marked improvement in mechanical properties particularly hardness and abrasive wear.*

**key words :** *Gray cast irons, Salt bath nitrocarburizing, Mechanical properties, Surface properties, abrasive wear.*

## 1. INTRODUCTION

Surface hardening of cast irons by nitriding/nitrocarburizing methods has recently and attracted renewed attention since these materials are often used to make large dies for metal-forming applications and mechanical engineering. Typical applications include cold drawing/extrusion dies plastic extrusion screws, guide ways, piston ring used for current marine diesel engines. Many studies have showed than the surface properties of gray cast irons can be improved by several processes like heat treatment, laser and nitriding/nitrocarburising [1-3]. Ferritic nitrocarburizing (FNC) is extensively used in the heat treatment industry as a surface hardening technique for applications where high wear, scuffing, and fatigue resistance irons are required [4-5].

Modification of surfaces by salt bath or gaseous nitrocarburizing is a process what is widely used in manufacturing of machine components and tools, since an improved surface hardness, fatigue strength and corrosion resistance at elevated temperatures, can thus be achieved at minimum distortion [6]. These processes are simple, cost effective, appropriate for parts made of case hardening steels, tool steels for hot work, high speed steels and cast irons, while also being environment friendly [7]. Ferritic salt bath nitrocarburizing is a thermochemical surface treatment during which nitrogen and carbon are supplied simultaneously to ferrous alloys surfaces at temperatures usually between 550°C to 580°C. Despite numerous publications on the technology of plasma and gaseous nitrocarburizing of ferrous alloys [8-9], but there are very few works devoted to salt bath nitrocarburizing of gray cast irons. The mechanical properties of cast irons are determined by its structure, especially by its graphitic component. The cast iron can be considered like a steel transfixed by the graphite that plays the role of the slashes weakening the metallic matrix of the structure. In this case, the mechanical properties depend the quantity, the size and the distribution of the graphite inclusions. However, gray cast iron contain graphite in different forms, which may

become detached from the matrix during machining. For this principal reason, the objective of this work is to protect these materials against the abrasive wear. The carbon and nitrogen atoms released by the decomposition diffuse into the cast iron and ultimately produce both the compound and diffusion layers in order to exhibit higher toughness, and also possess high wear resistance under dry or lubricating friction due to its hexagonal layered structure and its microporosity.

The objective of this work is to improve the surface characteristics such as wear resistance using salt bath nitrocarburizing process without post-oxidation of gray cast iron. The analysis and characterization are carried out using scanning electron microscopy, X-ray diffraction and Energy dispersive X-ray diffraction and mechanical measurements (microhardness Vickers, weight loss, surface roughness).

## 2. MATERIAL AND EXPERIMENTAL PROCEDURE

### 2.1. Material

The material used in the experimental work was a gray cast iron Ft25 type (Afnor norm) produced in industrial foundry of Tiaret (Algeria) and analyzed by spectrolab LAVMC11A type. The global chemical composition of the material studied is reported in table 1. Micrographic observations of this material revealed that the matrix was pearlitic- ferritic structure with a lamellar graphite.

**Table I:** Global chemical composition (weight percent) of Ft25 gray cast iron.

C	Mn	Si	S	P	Fe
3.93	0.68	1.68	0.051	0.009	bal.

### 2.2. Experimental procedure

In order to compare the abrasive wear between the samples treated and nitrocarburized, the specimens were heated to the austenitizing temperature of 830°C/1h, followed by quenching in oil and then tempered at 180°C during 1h. These conditions have been chosen in order to assure the best compromise between strength and ductility properties and also the relaxation of stresses required after quenching treatment. All experiments were carried out on cylindrical samples (50mm of diameter and 10mm of thickness) ground and polished up to a mirror surface. The nitrocarburizing process was carried out close to 580 °C in industrial molten salt bath consisting of 60% KCN, 24% KCl, and 16% K<sub>2</sub>CO<sub>3</sub> by weight for varying diffusion times from 2 up to 6h. After that a group of nitrocarburized samples was cooled in water to room temperature (classical salt bath nitrocarburizing process). After nitrocarburizing, perpendicular and bevel cross-sections of the nitrocarburized layers were prepared.

The perpendicular cross-sections were used for the observation of the microstructure by scanning electron microscope (Carl Zeiss U550). The microstructure on the cross-section of nitrocarburized samples was analyzed after metallographic preparation and etching with 3% NITAL (3% HNO<sub>3</sub> in ethanol). Microhardness profiles were measured on bevel crosssections, the distance from surface was corrected to the real distance on a perpendicular sample. The nitrated case depth was calculated from the microhardness profiles as a depth where the hardness is equal to the core hardness more 100 HV<sub>0.05</sub>. The hardness distribution profile of the resulting layers was established using a microhardness tester (ZWICK-ZHV10) with a load of 50 g for a dwell time of 15 s. In addition to the hardness, the surface roughness (Ra), showing the mean arithmetic surface profile deviation, was also measured with the

SURFTEST SJ-301 profilometer on all nitrided samples. In addition, XRD patterns were obtained using a diffractometer (Siemens D8 Advance), with  $\text{CuK}\alpha$  radiation and operated at 45 kV and 30 mA. A  $2\theta$ -scan was recorded within the range  $30^\circ$ – $100^\circ$ , with a constant stepwise increase of  $0.016^\circ/\text{sec}$ .

The abrasion resistance was determined under dry conditions, in air and at room temperature. The abrasive wear tests were conducted by means of a pin on disc [10-12]. Pinshaped specimens 10 mm in side were forced to slide on fresh 800-mesh abrasive paper with an applied normal load of 3 N and the sliding distance was defined as 900m. The paper was fitted on a steel disc rotating at a speed of 30 rpm as determined after using a polishing machine. This low angular speed is chosen to establish the relative wear of the different phases at the immediate surface layers. After a certain sliding distance, the specimens were removed and rinsed completely. The abrasion criterion retained in this study is the weight loss. [12]. An analytical microbalance accurate to  $10^{-3}$  g was used to measure weight changes.

### 3. RESULTS AND DISCUSSION

#### 3.1. Microstructure and phase composition of nitrocarburized layers

The microstructure investigation of the nitrocarburized layers shows that these layers are formed of two sublayers a compound layer and diffusion zone (Fig.1). In extremely surface, we observe a continuous compound layer ( $\epsilon$ -  $\text{Fe}_{2-3}\text{N}$  and  $\gamma'$ - $\text{Fe}_4\text{N}$ ) partially porous. This microstructure type is similar to the microstructure founded by E. Rolenski and al [13].

We can see significant penetration of compound layer to the diffusion zone. It's clearly observed than the continuous layer is formed between the graphite particle and matrix because the defects. The diffusion of oxygen leaded systematically in over layer a thinner oxide layer ( $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$ ) which exhibits extraordinary fatigue, tribological properties, and corrosion properties [14].

It means that the chosen nitrocarburizing conditions lead to some saturation of the surface layer and sublayer with nitrogen and carbon atoms. For this, the figure 2 shows the distribution of energy distribution of X-ray diffraction of elements such as carbon, nitrogen, oxygen and iron since the over surface to a diffusion zone. The diffusion zone is principally formed of ferrite, nitrides and carbides ( $\text{Fe}_3\text{C}$ ). These phases are present on the samples nitrocarburized at all applied conditions. For example, in figure 3(a,b) we shows the X-ray diffraction results where the peaks of  $\epsilon$ -  $\text{Fe}_{2-3}\text{N}$  and  $\gamma'$ - $\text{Fe}_4\text{N}$  are diffracted in several angles for a samples nitrocarburized at  $580^\circ\text{C}$  during 2h and 6h. We have observed than the depth of a compound layers prepared by salt bath nitrocarburizing at  $580^\circ\text{C}$  since 2 up 6h reaches a values varying approximately from 0.85 up to  $15\mu\text{m}$  and the total thickness of nitrocarburized layers changes respectively from 100 up to  $400\mu\text{m}$ .

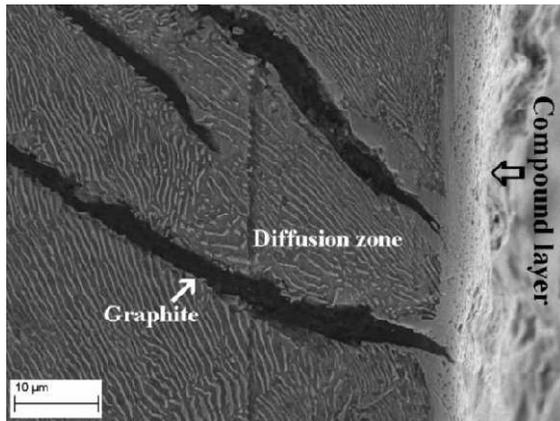


Figure 1. S.E.M showing the compound layer and diffusion zone of gray cast iron nitrocarburized at 580°C/6h.

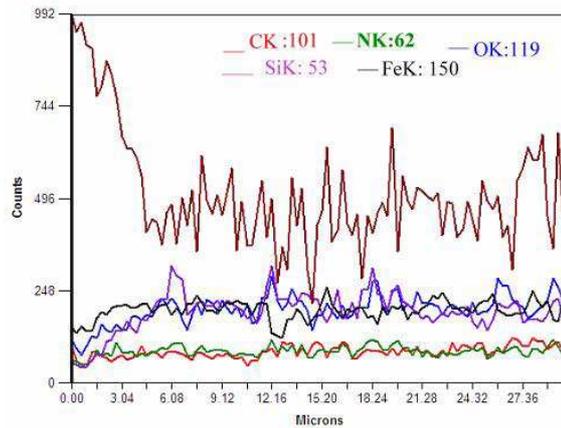


Figure 2. EDX curves of sample nitrocarburized at 580°C/6h.

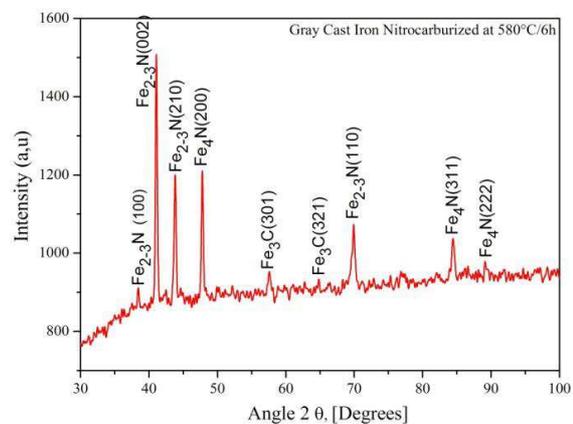
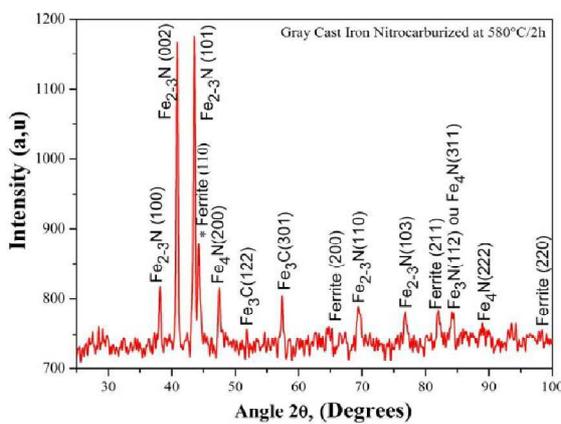


Figure 3 (a, b). XRD spectra : a) sample nitrocarburized at 580°C/2h  
b) sample nitrocarburized at 580°C/6h

### 3.2. Layer hardness and surface roughness

Figure 4 shows microhardness profiles obtained from cross-sections of different samples nitrocarburized. All samples show high microhardness values in the surface that drop decreasingly at the core interface to substrate microhardness values. It can be observed that higher surface hardness values are obtained for nitrocarburising temperatures of 580°C during 6h. The shape of the microhardness profiles of the hardened surface, at various exposure times, is almost similar. The microhardness is characterized by a decreasing gradient from the surface towards the core, which is associated with a change in nitrogen and carbon concentration.

For specimen nitrocarburized at 580°C/6h, at 10 µm from the surface, the hardness value is approximately 750 HV. Beyond this depth and up to 600 µm, this level decreased progressively to a value of 300 HV where it stabilizes definitively. The lower level of microhardness measured on the surface is due to the presence of porosities in the compound layer, which are noticeable in Fig. 1. This is a phenomenon that is peculiar to salt bath nitriding or salt bath FNC. According to figure 5 we can see that the difference in the diffusion time provoke a sensitive change in surface roughness. For nitrocarburized layers

formed at 580°C, the roughness varied from 0.44 to 0.83 μm when the deposition time increased from 2 up 6h. The results confirmed that the measured values are characteristics of the gray cast iron nitrocarburized and are in good agreement with literature [13-14].

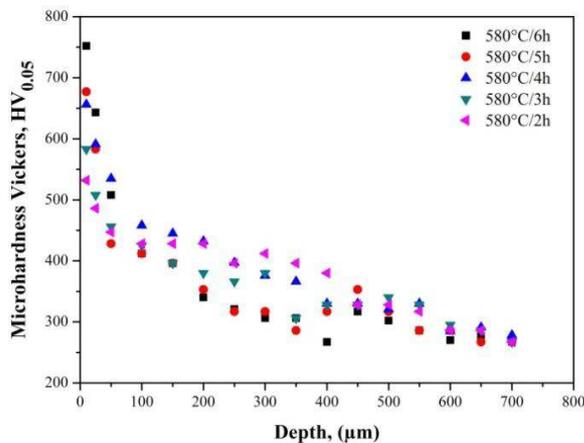


Figure 4. Microhardness distribution over the cross-section of salt bath nitrocarburized samples.

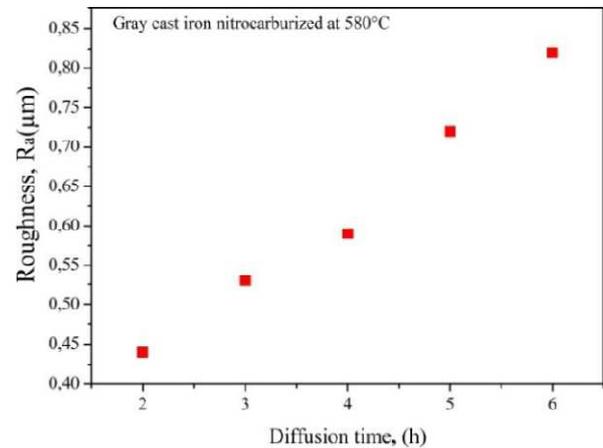


Figure 5. Variation of roughness as a function of the diffusion time.

### 3.3. Abrasive wear

The wear resistance depends mainly on the hardness of the diffusion layer, while the nature of the compound layer intervenes little because of its lower thickness. However, any important increase in hardness usually leads to an increased brittleness of the layer and thus deteriorating the wear behavior [15]. The  $\epsilon$ -phase has a strong wear resistance but its impact strength remains critically low. On the other hand,  $\gamma'$  phase showed little wear resistance and an appreciable resistance under impact loadings. Wear expressed as weight loss as a function of the sliding distance is presented in figure 6. It is observed that the curves (wear–distance) have the same trends and exhibit notably different wear rates according to the nature of involved phases. The results gotten agree besides well himself with the literature [16].

According to the existence of the different layers and their different wear behaviors, we divided every curve in 4 domains.

A first field corresponds to the existence of fine oxide layer on the surface. The presence of the latter is not identified by X-rays, but it is revealed by profil EDX spectra (Fig.2) where oxygen concentration is present in over surface. As a result, the presence of oxygen content in the outermost surface may be due to oxidation during the diffusion process and cooling. These oxide layers of higher hardness and lower adherence, being scaled very quickly to leave the first distances of sliding between 0 and 50 m show a wear rate of  $2.5 \times 10^{-4} \text{ g}\cdot\text{m}^{-1}$ . To 50 meters of sliding distance, in Figure 7a, one records the wear tracks corresponding to a compound layer and the non complete delaminating of the oxide layer. Beyond this distance, one notes the wear tracks of the compound layer and the apparition of the existence of diffusion zone (presence of graphite, see (Fig.7b)).

The second field corresponds to the compound layer and diffusion zone, which is extremely hard. The wear of this layer occurs at the distance of sliding of (50÷ 150) m thus showing a wear rate varying from  $1.5 \times 10^{-4}$  to  $3.5 \times 10^{-4} \text{ g}\cdot\text{m}^{-1}$  for the various samples. Considering the nature of the thick layers (iron oxides and compound layer), the best abrasive wear resistance is gotten in the nitrocarburized sample (580°C/6h). The micrographics clearly puts in

evidence, to 50 meters, one confirms that one is in the compound layer zone (Fig.7c). Dice that the sliding distance increases (150m) the layer begins to disappear (existence of the diffusion layer and the presence of graphite, see Figure 7d). The third zone refers to the thickest diffusion layer of (150 ÷ 600)  $\mu\text{m}$  and has the best wear resistance since the fine precipitation of nitrides and carbides are homogeneously dispersed in the ferritic – pearlitic matrix . It is generally accepted that the presence of precipitates such as carbides in a material will improve resistance to wear [17]. However, we can see also, for more 600 m of sliding distance, the wear rate of matrix is lower because the presence of graphite. Finally, the last field corresponds to the wear of the matrix and the weight loss for the various samples is almost the same a wear rate. Generally, at a load of 3N, the weight loss of the nitrocarburised samples is lower than tempered samples. It would appear that the wear behavior of the nitrocarburised samples was controlled mainly by the nitrocarburised layers.

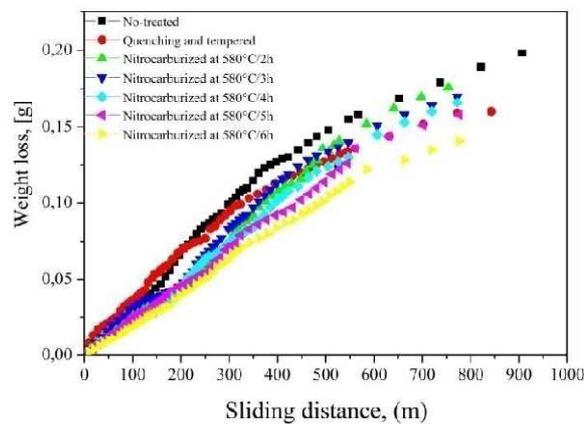


Figure 6. Weight loss results for various treated samples.

The hardness surface layers produced by nitrocarburizing process possess the improved abrasive wear resistance in comparison with the non-nitrided samples.

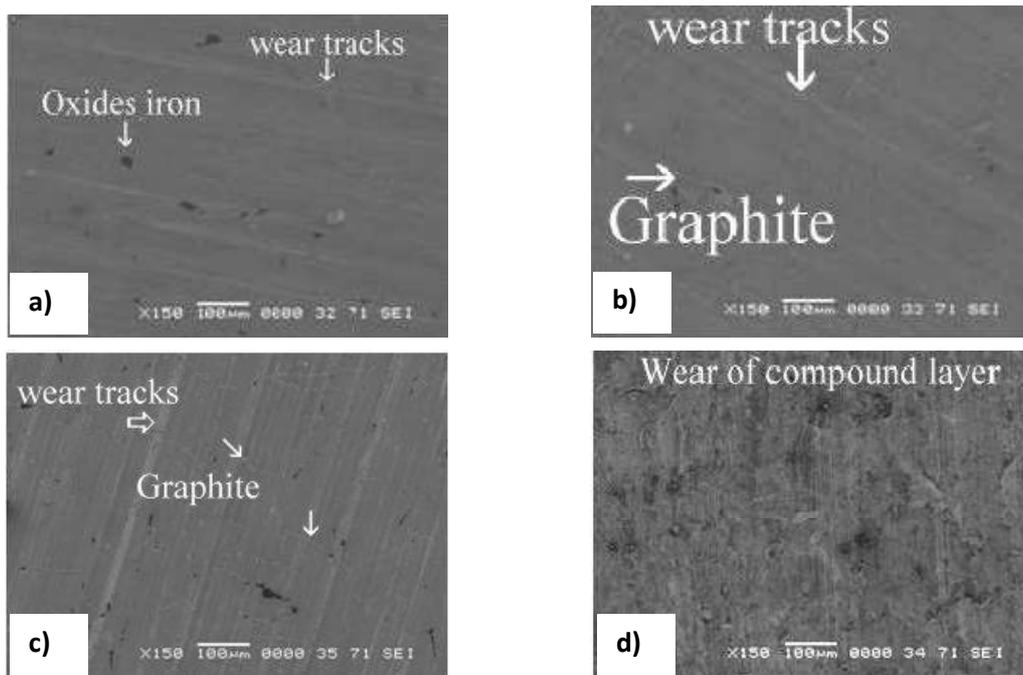


Figure 7 (a,b,c,d). S.E.M micrographs showing the abrasive wear mechanism of gray cast irons nitrocarburized after different sliding distances. (a,b) samples nitrocarburized 580°C/2h.

## 4. CONCLUSIONS

The following conclusions can be drawn from the present investigation:

Salt bath nitrocarburizing treatment is suitable for improving the mechanical properties of gray cast irons.

In salt bath, particularly, the compound layer is porous. Induced porosities strongly contribute to the occlusion of oxygen in samples tested. Thus, they will not produce satisfactory surface metallurgy. Thus, they will not contribute to the improvement of the properties such a friction coefficient and corrosion behavior.

The presence of high carbon content prevented not the diffusion of nitrogen and carbon. In gray cast iron will tend to produce more  $\epsilon$ -carbonitrides whose field of existence is wide, in the ternary system Fe-C-N It was also shown, during salt bath nitrocarburizing of gray cast irons, the presence of defects facilitates the formation in depth of compound layer between the graphite and matrix.

It was shown that a diffusion time has some consequences on the formation kinetics of nitrocarburized layers and surface roughness. Also, the time has a effect on the structural and mechanical properties of nitrocarburized samples. In the case of nitrocarburized sample at 580°C/6h, a lower weight loss in conjunction with an increased level of microhardness value is observed compared with the other diffusion time.

Compared with heat treatment and nitrocarburizing process results previously obtained, an important improvement of the mechanical properties is noted in terms of increased microhardness and a lower weight loss. The nitrocarburizing process, at 580°C/6h, presents the best compromise.

## REFERENCES

- [1] Jong-Hyun Hwang, Yun-Sig Lee, Dae-Young Kim, Joong-Geun Youn, Laser Surface Hardening of Gray Cast Iron Used for Piston Ring JMEPEG (2002) 11.
- [2] D. Wells, Ion Nitriding: Only the Best Case for Gas Compressors, Heat Treat. Prog., (2001), August/September.
- [3] O. D. Sokolov, O. V. Mannapova, A. I. Kostrzhyts'kyi, and A. P. Olik, Enhancement of the corrosion resistance of gray cast iron by iron nitriding, Materials Science, Vol. 42, No. 6 (2006).
- [4] B. Bhushan and B.K. Gupta : Handbook of Tribology : Materials, Coatings and Surface Treatments, cGraw Hill, NY (1991).
- [5] D. Pye: Practical Nitriding and Ferritic Nitrocarburizing, ASM International, Materials Park, OH (2003).
- [6] J. Michalski, E. Eunarska, J. Tacikowski, J. Tymowski, T.N. Tarfa, P.Wach, A. Dudek, The 9th International Seminar, Nitriding Technology (2003).
- [7] O. Schwerdtfeger, Über die Sicherheitstechnische Beurteilung von Tenifer- Anlagen der Degussa AG, Degussa AG (1985).
- [8] A. D. Sokolov, "Surface hardening of piston rings by nitriding in a glow discharge," Metalloved. Term. Obrab. Met N<sup>o</sup> 5, 42–44 (1982).
- [9] A. E. Rudyk and V. G. Kaplun, "Wearresistance of nitrided 45Kh steel and SCh18 cast iron in distilled water," in: Problems of Friction and Wear [in Russian], Issue 27, Kiev (1985).

- [10] R.Ipek,B.Selcuk,M.BKaramis,V.Kuzucu, A.Yucel, J.Mater.Process.Technol.(2000) 105,13.
- [11] M.Yan, W.Z.Zhu, Surf.Coat.Technol (1977) 91,183.
- [12] M.L.Fares,M.Z.Touhami,M.Belaid, H.Bruyas, Surface characteristics analysis of nitrocarburized (Tenifer) and carbonitrided industrial steel AISI 02 types, Surf. Interface. Anal (2009) ,41.
- [13] E.Rolinski, A.Konieczny,G.Sharp, Nature of surface changes in stamping tools of gray and ductile cast iron during gas and plasma nitrocarburizing, Journal of Materials Engineering and Performance (2009).
- [14] M. Zlatanovic, N. Popovic, Z .Bogdanov. Formation of magnetite overlayer on nitrocarburized low-alloy steel by plasma postoxidation, Surface & Coatings Technology (2004) 188–189
- [15] D.Duchateau; J.P.Peyre, Y.M.Chen, J.G.Pavy, Surfaces (1999),290 ,40.
- [16] S.Mohan,Ved Prakash; J.P. Pathak, Wear characteristics of HSLA steels, wear 252 (2000).
- [17] L.M.Hutchings,Friction and wear of Engineering Materials Tribology, London, Publication E. Arnold (1998).