An Investigation on the Usefulness and Performance of New Hot Working Tool Steel by Nitrocarburizing Process

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Salt bath nitrocarburizing effects on usefulness and performance of a new grade hot working tool steel close to as either chromium AISI H11/H13 are investigated. A continuous two-step treatment is performed, consisting in hardening sequence (i.e. austenitzation-1050°/15 min, quenching-oil medium and twice tempering-500 and 600°C/2 h) followed by a salt bath nitrocarburizing process at 580°C for various processing times. Prior treatments yield a reliable tempered martensitic microstructure without bainite, in which are embedded complex carbides without any retained austenite content, achieving satisfactory hardness value of 53HRC. Subsequent thermochemical treatments allow relative relevant properties such as surface hardness and wear behavior through formed layers that are characterized by their basic properties (i.e. thickness, formed phases, hardness distributions and redistribution of alloying elements in the nitrocarburized layers). Based on in-house experimental data, it can be outlined that salt bath nitrocarburizing process is suitable for improving surfaces characteristics of the as-studied treated material, in a shorter time with minimal cost compared to other similar processes. Metallurgical evaluations are carried out using metallographic techniques, optical and scanning electron microscopy equipped with an energy-dispersive X-Ray spectrometer as well as X-ray diffraction techniques. Mechanical properties are achieved mainly by standard hardness and wear tests. [DOI: 10.1380/ejssnt.2012.1]

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I. INTRODUCTION

The application field for hot working tool steels is extensive and manufactured tools are used in diverse areas such as working or forming metals at high temperature (i.e. extrusion dies, die-casting, forging die etc.). In practice, tools are exposed to high pressures, elevated temperatures, and both mechanical and thermal fatigue [1], as well as wear mechanisms [2]. In view of that, such effects act to an increased susceptibility to damage, resulting in limitation on material life. It is well known that properties' profile of the tool material greatly influences its lifetime. Among these properties (e.g. high tempering resistance, thermal shock resistance, dimensional stability, high hardenability, high-temperature toughness and wear resistance), some basic and exclusive ones are very significant for almost all applications (i.e. toughness and hardness). These properties depend on proper selection of a steel grade and treatment parameters, which play an important role in the resulting manufacturing quality. However, these properties are often contradictory and are impossible to fulfill in only one type of steel at the same time and in the same manner. The challenge is to find the best compromise between material and process combination for each particular case. For this purpose, a large variety of standard hot working tool steels are used (e.g. AISI H10-H19 with a series of commercial special ones), while AISI H11/H13 steel grades are the most widely exploited in industry and this is confirmed by the availability of an extensive body of literature [3, 4].

In practice, to ensure tool steel's usefulness requires many protection applications. The proposals, going from bulk thermal treatments to surface modifications, can be employed to increase the surface hardness and wear resistance of tool steel components. One approach is to use a grade of steel that already contains sufficient carbon and alloying elements to provide the required surface after conventional heat treatments. Such treatments, including austenitizing, quenching and tempering, are the most pretenders since they have been developed further based on detailed research and practical studies [5–8]. Besides, empirically created hot working tool steels with optimum composition being so numerous, have been and continue to be tested and characterized through several research projects [9–11]. According to specific applications, as earlier quoted, they are expected to lead to hardness levels in the range of 43-52, 44-50 and 40-55HRC for extrusion dies, die-casting and forging dies, respectively [12]. The associated relevant factors, which can be monitored, are suitable preheating, austenitizing temperature, quenching rate, tempering temperature, number of tempering cycles as well as soaking time. Owing to severe service conditions, additional surface modifications of components are frequently required in order to enhance their lifetime by improving strength, tribological properties as well as corrosion resistance [13]. Commonly, this revolve the increasing case hardness by diffusion of carbon and/or nitrogen into the surface, using thermochemical treatments such as carburizing [14, 15], carbonitriding [16, 17] and nitrocarburising [18, 19] processes.

Salt bath nitrocarburizing (Tenifer®) is diffusion-based surface treatment that combines the effects of nitriding and carburizing. It is a favorable candidate for

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improving hardness, wear resistance and is widely used in industry because it is simple, cost effective, and appropriate for hot working tool steels [20]. In opposition to the earlier mentioned processes, the low process temperature of \( \sim 580^\circ C \) is considered as more advantageous since it does not undergo structural changes in the core [21], promoting, thus, both minimal dimensional changes and distortions as well as short processing times of the treated components. In addition, finished parts could be used without any post-machining and the possible control of bath composition has the potential to eliminate virtually any disadvantage of the process (e.g. ecological requirements). The involved modifications consist in the simultaneous introduction of carbon and nitrogen into the steel in ferritic condition. As a result, the formation of two distinct and attractive layers could be achieved (i) the compound layer of epsilon carbonitrides \( (\text{Fe}_2 \ldots \text{C}, \text{N}) \), improving the wear resistance [22], and (ii) the diffused layer \( \alpha-(\text{Fe}, \text{N}) \), resulting in enhancement of fatigue strengths [23]. Some of the global increased hardness of the treated layer is due to a diffusion zone, especially in the more highly alloyed steels with strong nitride formers. In the other hand, the presence of porosities, formed in the outer zone of the compound layer, may be favorable since it promotes absorption of a lubricant or corrosion inhibitors [24], which is flattering in the case of surface subjected to friction wear or corrosion.

Although, there are a large number of published works on nitrocarburizing of standard hot working tool steels, little has been reported on modified tool steels using salt bath process. Thus, this paper took a systematic research on such items in order to demonstrate the effectiveness of as-studied new hot working tool steel, comprising higher carbon content and lower silicon one compared to existing standard steels. For this purpose, attempts have been made in the direction of the application of different procedures of treatments, including appropriate heat treatments and a subsequent salt bath nitrocarburizing process. Results will be presented paying specific attention to the effects of chemical composition and parameters process on the microstructure, formed phases, layer depths, hardness, and wear resistance. It is hoped that this overview will lead to obtain competitive materials having satisfactory tool life and higher productivity in a wide range of applications. A detailed phase characterizations in terms of chemical composition, formed phases and microstructures are undertaken mainly by optical microscopy (OM) and scanning electron microscopy (SEM) as well as X-ray diffraction techniques (XRD). Mechanical properties are evaluated by microhardness and abrasive standards tests.

II. MATERIALS AND EXPERIMENTAL PROCEDURES

A. Material

The material considered in this investigation is a modified alloy hot working tool steel (supplied by the company SA. Euro Metal Service (Schilde, Belgium). Its chemical composition, identified by the THERMO SCIENTIFIC ARL 4460 optical emission spectrometer (OES), is reported in Table I. Compared to standard steel grades (i.e. AISI H11 and H13 steels), it discloses some difference in carbon, vanadium, nickel and silicone contents whereas the percentage of the other element contents are approximately similar.

B. Treatments

Preheating treatments (i.e. hardening and tempering) are achieved in a laboratory scale since thermochemical treatments are carried out in an industrial plant facility (EMO, Constantine, Algeria). For such intended treatments, cubic samples \( (10 \times 10 \times 10) \text{ mm}^3 \) in size are prepared and then subjected to an annealing operation to eliminate residual stresses that resulted from pre-machining and to give an appropriate microstructure for subsequent hardening. Afterwards, specimens are successively austenitized, quenched and twice tempered in a furnace chamber. Finally, salt bath nitrocarburized treatments are achieved at 580°C for different holding times, according to both treatment cycles and treatments parameters that are presented in Fig. 1 and Table II, respectively.
TABLE I: Chemical composition of as-received steel in comparison of standard hot working tool steels (wt.%), Fe balance.

|                | C  | Mn | Si | Ni | Al | Cr | V  | Ti | Mo |
|----------------|----|----|----|----|----|----|----|----|----|
| As-received    | 0.52 | 0.42 | 0.55 | 0.22 | 0.03 | 5.20 | 0.34 | 0.004 | 1.10 |
| Standard 1.2343/H11 | 0.38 | 0.40 | 1.00 | —   | —   | 5.10 | 0.40 | —   | 1.25 |
| Standard 1.2344/H13 | 0.40 | 0.40 | 1.05 | —   | —   | 5.15 | 1.00 | —   | 1.35 |

TABLE II: Treatment parameters and specimen designations for various investigated specimens.

| Treatment Designations       | Process and treatment parameters | Cycles | Specimen Holding time | designations       |
|------------------------------|----------------------------------|--------|-----------------------|--------------------|
| Heat treatments              | Soft Annealing                   | 550°C + 880°C Furnace (1/3) h | A1                  |
| (Hardening)                  | Austenitizing + Quenching        | (900-1000)°C in Oil            | Q2                  |
|                              | First tempering                  | 600°C in Air                    | QT1                |
|                              | Second tempering                 | 25°C gradation in Air           | QT2                |
| Thermochemical treatments    | Salt bath nitrocarburizing Tenifer®: | 570°C | Oil                    | NC2                |
| (Nitrocarburizing)           | Salt bath components: cyanides   | 4 h                           | NC4                |
|                              | N₂ contribution: Cyanates        | 6 h                           | NC6                |
|                              | Decomposition by cyanide: Oxidation. | 8 h |                                | NC8                |

C. Characterization

Prior to optical observations, surface preparation consisted in mechanical grinding using 250 to 1200-grit mesh and subsequent polishing down to a final step of 1 μm diamond pastes. After ultrasonic cleaning in ethanol, samples are etched in a 3% nital solution at ambient temperature.

Metallographic investigations are achieved using optical microscope type GX.51 Olympus as well as both scanning electron microscopes JEOL SJM-6500F with Energy Dispersive X-ray Spectrometry attachment (EDS) and FESEM ULTRA 55–ZEISS with integrated EDX spectrometer (THERMO-SCIENTIFIC) types to determine the elemental distribution curves for nitrocarburized specimens. Then, volume fractions of formed phases (retained austenite, martensite and carbides) are determined by the Guinier’s method [25], using a PHILIPS PW1730/10 diffractometer operated at 40 kV and 200 mA, with a cobalt anticathode of λKα = 0.179026 nm. The same diffractometer is used to determine formed phases of nitrocarburized specimens.

Hardness tests of the hardened samples are performed by means of the Rockwell method using a universal machine of WOLPER type machine since Vickers microhardness profiles of the resulting nitrocarburized layers are obtained from the cross sections using microhardness IMT-3 (IIOMO) tester. Measurements performed with a load of 0.49 N (50 g) for a dwell time of 15 s, yield the assessment of layer thicknesses and precise measurements are supported, in addition, by the use of the IMAGE TOOL SOFTWARE STIRLING TECHNOLOGIES, INC.

Abrasion criterion measurements adopted in this study are based on the weight loss method [26] and the resistance to abrasion is determined under dry conditions, in air and at room temperature. The abrasive wear results are obtained by means of a pin-on-disc test [18], where specimens are forced to slide under a normal applied load of 3.47 N on a fresh 800-mesh abrasive paper, fitted on a steel disc of a polishing machine, rotating at a speed of 12 cycles /min. In this study, an attempt in discarding adhesive wear is achieved by the application of both low contact pressure and low angular speed. This later is chosen in order to establish the relative wear of the different phases at the immediate surface layers for each treatment time. After a prescribed sliding distance, samples are removed and completely rinsed. An analytical microbalance accurate to 10-3g is used to measure weight changes.

III. RESULTS AND DISCUSSIONS

A. Heat treatment

According to the suggested thermal cycle treatment shown in Fig. 1, preliminary heat treatments (i.e. hardening) of specimens are performed in order to achieve a tempered martensitic microstructure with a maximum hardness that should yield an improved wear resistance [27]. The right choice of austenitising temperature, soaking time and quenching medium are the basis in getting optimal properties such as hardness and toughness after tempering process.

Figure 2 shows hardness results performed in-house vs. treatment temperatures of the annealed steel. In Fig. 2(a), hardness results are assessed in function of austenitization temperatures in the range (900-1100)°C with a step of 50°C for a soaking time of 15 min. It can be seen that the hardness of as-studied steel increases with quenching temperature. This is concomitant with
the integration of alloying elements. It is also noticeable that a maximum hardness value, close to 57 HRC (“Q1” sample), is obtained for 1050°C since it can be changed by subsequent tempering treatments with regard to the achievement of required properties for a specific application. Such result agrees with earlier reported studies affiliated at H11 and H13 steel grades [8, 28, 29]. Beyond 1050°C, it is observable that the increase of the austenitizing temperature yields an important hardness drop close to 42 HRC, probably due to the relative degree of austenite grain coarsening. Afterward, “Q1” sample is subjected to the first tempering operation for 2 h, in the temperature range (450-625)°C, with gradation of 25°C. Accordingly, Fig. 2(b) exhibits the temper resistance, assessed from the tempering curve for hardness vs. tempering temperatures. It can be seen that, in the range (475-500)°C (broken line), the hardness rises from 51 to a maximum value up to 54 HRC. This increase can be ascribed to three distinct transformations occurring during the tempering operation: (i) destabilization of retained austenite, which is sensitized by tempering, (ii) transformation in tempered martensite, (iii) fine carbides precipitation, which may be associated to the secondary hardness mechanism. These results are in good agreement with those of Dobrzanski et al. [30] on H13 steel leading to an optimal hardness of 53.5 HRC after quenching and tempering at 1060 and 510°C, respectively. Beyond the tempering temperature of 525°C, hardness exhibits a noticeable fall down to 43 HRC, for tempering temperature of 625°C. The increase of the tempering temperature above 500°C results in an initiation of the recrystallization of martensite and a coagulation of newly created alloy carbides that could explain such considerable hardness drop. At this step, the lower silicon content (∼0.55%) can have a favorable effect on the properties of hardened and tempered as-studied tool steel. Accordingly, Delagnes et al. [11] stated that higher silicon has a negative effect on the AISI H11 steel, as it shifts the secondary hardening peak towards lower tempering temperatures. As a result, reducing the silicon content may outcome in a possible use of the tool for higher service temperature (an excess temperature from 20 to 30°C). Besides, despite of the upbeat effect of silicon content that consists to high temperature antioxidant capacity, it has been gradually recognized that the low silicon has as effect to reduce material segregation, to improve crystallization, microstructure of austenite grain refinement, toughness (refinement of the carbides component) and thermal fatigue properties [31].

Figure 3 allows a better view of the detailed microstructure transition under the effect of the prescribed heat treatment cycle. Commonly, a balanced chemical composition of carbide forming elements, such as chromium, molybdenum and vanadium, acts to provide an excellent soft-annealed initial structure for the subsequent tool hardening. Figure 3(a) corresponds to an annealed microstructure of so-called “A1” sample, showing a homogeneous precipitation of globular carbides embedded in a ferritic matrix. Such configuration is associated to the optimal sought structure. The corresponding measured hardness value is (∼180-210) HB, which is concomitant with a good machinability. X-rays spectra of Fig. 4(a), determining the sequence of induced precipitation, reveals the presence of M7C3 (M: Fe mainly), M23C6 (M: Cr mainly) and a small ratio of M7C3 (M: V mainly). Figure 3(b) exhibits the optical microstructure of the “Q1” sample after quenching at 1050°C for 15 min. It comprises lath martensitic structure, partially twinned connected to a small fraction of retained austenite and carbides. The average diameter of the primary austenite grain size, being about 15 μm (ASTM F112-74), allows obtaining advantageous mechanical properties [30], despite the lower vanadium content, which even remains sufficient to prevent grain coarsening.

Figure 4(b) displays X-ray spectra of quenched and tempered ("QT1") sample, showing a homogenous precipitation of globular carbides embedded in a ferritic matrix. Such configuration is associated to the optimal sought structure. The corresponding measured hardness value is (∼180-210) HB, which is concomitant with a good machinability. X-rays spectra of Fig. 4(a), determining the sequence of induced precipitation, reveals the presence of M7C3 (M: Fe mainly), M23C6 (M: Cr mainly) and a small ratio of M7C3 (M: V mainly). Figure 3(b) exhibits the optical microstructure of the “Q1” sample after quenching at 1050°C for 15 min. It comprises lath martensitic structure, partially twinned connected to a small fraction of retained austenite and carbides. The average diameter of the primary austenite grain size, being about 15 μm (ASTM F112-74), allows obtaining advantageous mechanical properties [30], despite the lower vanadium content, which even remains sufficient to prevent grain coarsening.

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data for volume fractions of ferrite (martensite), retained austenite and carbides formed by quenching at 1050°C and twice tempering for 500 and 600°C, respectively, obtained by means of Guinier’s method [25]. Results associated at “Q1” sample, points out that volume fraction of ferrite (martensite), retained austenite and M23C6 type carbides are 96, 4 and 2%, respectively. This is indicative of a significant structural hardening caused by the martensitic transformation and the satisfactory dissolution of carbides under the prescribed high austenitizing temperature. Accordingly, it is well known that the temperature at which austenite starts to transform into martensite on quenching (Ms) is a function of a chemistry of a material. As a result, a decrease of transformation points Ms and Mf may occur. Results provided in earlier work [6], allowed to assess Ms temperature by means of the Steven and Haynes’ formula [34], which is the most indicated because it can be used for steels containing up to 0.6% maximum of carbon content. Besides, relations defined by Koistinen and Marburger [34] could also provide the untransformed austenite fraction related to both Ms and Tq (quenching) temperatures. However, it is worth mentioning that in general, Mf may not correspond to 100% martensite, because some retained austenite might be present [35]. The computed value that gives an austenite amount of ~4.67% almost agrees with measured value of ~4%, while the one of martensite is ~95.33%. This feature can be linked to the higher quenching rate, which has a critical significance on microstructure shaping, final working tool properties and its extended service life. This fact is well corroborated by Mayer et al. [36], stating that pure martensitic microstructure resulted in the highest toughness value and a rapid quench may avoid the formation of bainite, achieving thus a relevant maximum hardness. However, it is important to point out a major difficulty that consists in possible appearance of hardening cracks and some distortions in the quenched samples due to a rapid quench (oil medium). In some cases, a martempering process is advisable to reduce these risks.

Because of hardened steels are not satisfactory materials for most applications, a subsequent tempering treatment is required to obtain a tempered martensite microstructure with appropriate properties for industrial purposes. During tempering, some transformations occur in one part of the martensite and the second in the retained austenite, resulting in secondary hardening effect. Figure 3(c) reveals the optical microstructure of “Q1” sample after tempering at 500°C for 2 h. It can be noticed the disappearance of martensite needles that are changed in a newly tempered martensite (secondary martensite) composed of the wider laths than those of formed ones in “Q1” sample. At this stage, dislocations are pinned by carbon atoms, which have a strengthening effect on the martensite. Besides, the observed sensitive decrease in retained austenite content from 4% to 2% could be connected to a slight development of M23C6 carbides from 2% to 3%. It is well known that precipitates are the most relevant microstructural constituents with respect to hardness and thermal stability of the material. Since the mechanical properties of such materials strongly depend on type, particle number, density size and lattice structure of the existing precipitates, an extensive characterization could be completed, in perspective, by the use, for in-

**TABLE III: Volume fractions results of formed phases for hard-ened specimens using X-ray diffraction technique “Guinier’s method” [25].**

| Formed phases (%) | Q1 | QT1 | QT2 |
|-------------------|----|-----|-----|
| Carbides          | 2  | 3   | 3   |
| Feγ               | 94 | 95  | 97  |
| Feo               |    |     |     |

tempered samples, pointing up that retained austenite produces a diffraction peak at different locations than ferrite, due to its structural difference from other phases in steel. For “Q1” sample, only M23C6 chromium carbides that may have molybdenum and vanadium dissolved in them are disclosed while the ones of vanadium are not revealed. The disappearance of such carbides precipitation, caused by both higher quenching temperature of 1050°C and a relative higher cooling rate (oil bath) is probably not as harmful as first implied, since during the subsequent temper, the maximal precipitation may occur, thereby, yielding the secondary hardening. A fewer vanadium content of the studied steel (~0.35%) may also not be much of a problem, since it is sufficient to avoid the formation of undesirable in dissolved carbides which may remain along prior austenite grain boundaries throughout the thermal processing of the material. Commonly, the prescribed higher austenitizing temperature of 1050°C has the potential to give a better dissolution of the primary alloy carbides present in the annealed state, especially vanadium rich carbides [32, 33].

Table III is a summary of X-ray and electron diffraction

**FIG. 4:** XRD patterns of as-studied steel at various treatment states; (a) “A1” sample; (b) “Q1”, “QT1” and “QT2” samples.
stance, of a high-resolution method such as transmission electron microscopy (TEM) and atom probe tomography (APT) [37].

For most hot working tool steels, a second tempering is required in order to improve both toughness and thermal stability of the secondary tempered structure. Figure 3(d) shows the optical microstructure of “QT2” sample undergoing a secondary tempering at 600°C for 2 h. The choice of this temperature is justified by the fact that the tool material should not be tempered at a temperature lower than the operating temperature. It is worth mentioning if the secondary tempering is performed at a temperature above 600°C, it then allows to the coalescence of M23C6 precipitates departure [38]. The recorded hardness value is 53 HRC, which is favorable to shock resistance for any application. The laths of newly formed martensite, having 0.1-2 μm of width and 0.5-15 μm of length, are wider than the martensite ones that are formed in “QT1” sample. These values agree with those obtained on H11 steel by Delagnes in a previous study [39]. At this stage, volume fraction of retained austenite decreases from 2 down to 0%, while the carbides one stays at a level of 3% and remains the same as for the “QT1” sample. According to Fig. 4(b), it can be noticed that the Fe-peak intensity of “QT2” sample is greater than those of both “QT1” and “QT1” samples. This feature can be ascribed to the presence of tempered martensite, resulting of the austenite transformation, which have as effect to promote slighter network distortions.

As it has been already noticed on Fig. 3(d), optical microscopy does not yield the precise determination of the carbides presence in martensite matrix, due to its limited resolution. Therefore, the individual microstructural features of the tempered “QT2” sample are characterized by SEM microscopy and EDS microanalysis, as depicted in Fig. 5. Accordingly, the marked area in Fig. 5(a) shows carbides with 0.2 to 1 μm in size, corresponding undoubtedly to M23C6 (Fig. 5(b)), where M is chromium mainly: ~20.71 wt.% which may include both molybdenum (~1.79 wt.%) and vanadium (~2.63 wt.%) dissolved in them. The depicted relative extent of silicon content (~0.88 wt.%) is probably owed to the abrasive paper (SiC), at the time of the polishing operation. As, it can be obvious, second tempering yields spheroidized carbides which is indicative of suitable toughness.

B. Salt bath nitrocarburizing treatment

Figure 6 shows typical morphologies of the various salt bath nitrocarburised layers under the effect of exposure time on the layer thickness. Three regions can be, easily, distinguished that are the compound layer, the diffusion zone and the core. Global nitrocarburized depths, ranging from 68 to 141 μm for prescribed treatment times of 2, 4, 6, and 8 h, were precisely assessed thanks both Image Tool Software® and microhardness profile of Fig. 7. Conventionally, it is well known that global layer thickness is defined as the distance between the surface and the layer having a hardness corresponding to that of the core increased by 100 HV [40]. As it is expected, the increase in nitrocarburizing yields a relative deeper diffusion zone whereas compound layer thicknesses do not undergoes a significant change. Obtained lower values of compound layers (8-13) μm point out that corresponding depths are shallower than the ones of plain carbon materials, which can be ascribed to the effect of high alloying elements content [21]. Besides, it is admitted that thinner compound layers are able to prevent crack initiation [41].

According to the X-rays spectra of Fig. 8, formed phases consist mainly of Fe3O4 oxides, mixture of ε-Fe3N-γ'-Fe2N nitrides, Fe3o and (Fe, Cr)23C complex carbides whose proportions are in close relationship with the exposure time. Additional peaks of Fe3O4 rise with increasing exposure time since the ones of Fe3C tend to be indiscernible because of the limit of X-rays penetration within specimens. Besides, it is well noticeable that for both NC2 and NC4 samples only peaks corresponding to the single-phase ε-Fe3N are found. Indeed, with regard to Fe-N-C diagram, it is expected to have the ε-phase as dominant because the process method chosen (carbon potential) and the higher pre-existing carbon content (0.52%) of as-studied steel. However, with increasing treatment time, gamma'-Fe2N phase starts to develop in NC6 sam-

![FIG. 5: SEM analysis of “QT2” sample; (a) microstructure; (b) EDS analysis.](http://www.sssj.org/ejssn)
FIG. 6: Cross sections of nitrocarburized samples showing the white layer (top), the diffusion zone (dark) and the core below the diffusion zone.

FIG. 7: Microhardness profiles of nitrocarburized specimens.

perm for attaining the maximum in NC8 sample. Such behaviour can be explained by the depletion of carbon, yielding more carbonitrides with alloys elements. Thus, layers with different phase compositions can be obtained on the surface of components by changing only one process parameter such as duration while the temperature is maintained as constant.

Figure 9 depicts the SEM micrographs of NC4 sample in which the share of the compound layer is observable in more details (Fig. 9(a)). The compound layer remains unetched in nital and appears white under the microscope. In its outermost area, open porosities are noticeable and can have as effect to strongly contribute to the occlusion of oxygen, allowing thus better corrosion behaviour of treated samples [13]. Below the compound layer is the diffusion zone that consists mainly of ferrite (martensite) and globular alloyed carbides of (0.3-0.8) µm in average size and carbonitrides. This fraction is related to a zone of strong precipitation (instantaneous precipitation reaction). Such types of precipitation are likely to generate an important hardening mechanism. The precipitates formed with a specific volume greater than that of the ferritic matrix, will cause swelling thereof inducing a field of compressive stresses, which is indicative of suitable fatigue resistance [42]. Carbonitrides may undoubtedly exist in conformity to the existence of an enhanced amount of carbonitride-forming elements, despite the difficulty of their identification by the method of x-ray diffraction. In fact, taking account the high carbon content of 0.52%, the elevated capacity of tempered martensite has the potential to dissolve alloying elements, acting to the formation of such carbonitrides. In other terms, the dissolution of submicroscopic carbides outcomes from the grain boundary reactions between the migrating alloy nitride forming elements and/or carbon and the diffused nitrogen atoms. Figure 9(b) represents the microstructure of the core comprising a tempered martensite that remains unaffected by the subjected ferritic treatment.

Figure 10 displays the evolution of elemental profiles of nitrogen, carbon, oxygen, iron, molybdenum, and chrome through NC4 sample. Due to the oxidation reaction of the iron with the absorbed oxygen, the appearance of the higher oxygen level, at the extreme surface, may indicate the presence of a fine oxide layer. Because of the ability of oxygen to fill outer porosities present in the compound layer, two different decreasing rates of oxygen are observed. The first one corresponds to the porous zone, which extends up to 3 µm in depth, while the subsequent second one is characterized by a relative abrupt
fall, reaching the starting of the diffusion zone. Beyond this interface, oxygen displays a relative steady state towards the substrate. Likewise, carbon profile discloses a similar trend than that of oxygen, exhibiting a relative larger peak at the outermost of the surface followed by a sharply drop. This decrease might be due to a large concentration of chromium underneath the top surface. The high amount of carbon content (0.52%) of the material can have a significant influence on the absorbed carbon from the carbonaceous medium [43]. Thus, an enrichment of carbon occurs at the compound layer-diffusion zone interface, and a larger one through the diffusion zone. Carbon is pushed ahead in front of substrate and its redistribution permits to achieve the formation of both alloy nitrides/carbonitrides and precipitates, as it can be ascertained by the profile concentration of chrome element. Nitrogen concentration starts to increase gradually, depicting a maximum peak at the outermost compound layer followed by a slightly decrease towards the diffusion zone. Then, first, it exhibits a linear distribution profile (steady state) which corresponds to the zone of strong precipitation (i.e. the first fraction of the diffusion zone). Finally, it accuses a relative abruptly drop, characterized by an exponential profile, which is characteristic of usual diffusion mechanisms.

Microhardness profiles of nitrocarburised samples as a function of a depth for prescribed processing times are plotted in Fig. 7 whereas the corresponding results are summarized in Table IV. A relative decrease gradient from the surface towards the core is easily observable which can be associated with a change of carbon concentration (Fig. 10). For all treated samples, because of the presence of porosities induced in the compound layer, lower levels of microhardness measured at the surface are probably due to both “sinking effect: porosities” and “edge effect”. The maximum microhardness achieved at the surface lies in the range (1010-1200) HV0.05, with highest and lower values being recorded for NC4 and NC2 samples, respectively. Thus, the increase of surface hardness yield a better load support of the base material depicting hardness values in the range (520-550) HV0.05. Such results are indicative of no significant change occurring after nitrocarburizing treatment because of the lower process temperature with regard to the tempering temperature of earlier prescribed treatments (20°C in excess). As a result, both microstructure and hardness of the core material are likely to be unchanged. Like the case depth, surface hardness is strongly connected to the steel grade. In fact, it is well known that the increase of the alloying element content results in higher hardness values. More to this point, the introduction of nitrogen and carbon is also known to increase the hardness of materials, particularly for as-studied steel containing 0.52% carbon content. This fact is well corroborated by hardness profiles, which are in close relation to those of elemental concentration profiles, as it can be observable in Fig. 10.

Characterization of the relationship between nitrocarburizing treatment parameters (i.e. treatment time), formed phases and tribological behaviors of the treated layers is decisive in the ensuring the usefulness of components. Wear, expressed as weight loss in function of the sliding distance for studied specimens is plotted in Fig. 11. As it can be observed, profiles of weight loss have almost the same increasing trend and can be subdi-
FIG. 10: Elemental concentration profiles of nitrocarburized "NC4" sample.

TABLE IV: Layer thickness, hardness and weight loss results for various investigated specimens. Incertitudes measurements are ±1, ±5 and ±10−3, respectively, and global sliding distance for nitrocarburized samples is 106 m. Conversion of hardness values (DIN50150).

| Properties                          | Hardening | Nitrocarburizing |
|-------------------------------------|-----------|------------------|
| Sample codes                        | A1        | Q1               |
| Compound layer (μm)                 | —         | —                |
| Global layer (μm)                   | —         | —                |
| Top surface hardness (HV₀₀₅)        | —         | —                |
| Core hardness (HV₀₀₅)               | —         | —                |
| Maximum hardness (HV₀₀₅)            | —         | —                |
| Average hardness (HV₀₀₅)            | ~210 HB   | 57 HRC           |
| Global weight loss (10⁻³ g)         | —         | —                |
| Global wear rate (10⁻⁴ g·m⁻¹)       | 2.40      | 1.69             |

FIG. 11: Wear behavior of nitrocarburized samples.

vided into four zones. A first zone ‘a’ laying from 0 to 5m corresponds to a fine oxide layer present on the surface for all investigated samples. Such phase-layers, identified by both X-rays spectra (Fig. 8) and elemental concentration profiles in Fig. 10 for NC4 sample for example, are scaled in a very short time due to their both lower hardness and adherence. The assessed corresponding wear rate values are 4.27, 8.54, 13 and 4.27×10⁻⁴ g·m⁻¹ for NC2, NC4, NC6 and NC8 samples, respectively. The second field “b” is related to the compound layer that is extremely hard. The wear of these layers occurs at the distance of sliding of (5-25) m, showing an increase in wear rate varying from 0.35×10⁻⁴ to 3.7×10⁻⁴ g·m⁻¹, in function of exposure time. Accordingly, it can be worth noticed that both NC2 and NC4 samples exhibit the best wear resistance, caused by the presence of monophase ε-Fe₃N that have a relevant wear resistance due to the non-metallic character of the compound layer comprising hard nitrides [43]. The third zone “c” corresponding to the sliding distance in the range (25-69) m, presents the best wear resistance for NC4, NC6 and NC8 specimens, in conformity with the thickest diffusion layers when the nitrocarburizing time increases. At this stage, the fine precipitation of both nitrides and carbonitrides, homogeneously dispersed in the ferritic matrix, may improve wear resistance. For a given nitrocarburizing time each NC4, NC6 and NC8 samples shows a relative lower wear rate value in comparison with those corresponding to the compound zone. These results agree with previous work indicating that the wear characteristics depend on the hardness of deeper diffusion zone [44]. However, for NC2 sample, the opposite phenomenon is observed since the wear rate value (2.47×10⁻⁴ g·m⁻¹) related to the diffusion zone is extremely higher than the one of compound layer (0.35×10⁻⁴ g·m⁻¹) in spite of its lower hardness. These results indicate that the wear characteristics of the compound layer do not depend on its hardness [44], but on the wear mechanism involved [21]. The paramount wear resistance of the compound layer of NC2 sample can be explained mainly by the thinner corresponding diffusion zone and by its composition, consisting in a predominantly epsilon nitrides-phase. In addition, the existence of a relative jagged interface compound layer-diffusion zone (Fig. 9) may also promote its corresponding decrease of wear rate. These observations are consistent with those of Krishnaraj et al. [45], stating a resistance of the compound layer to spalling, under effect

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/) 9
of such interface feature. Finally, the last field “d” corresponds to the wear of the matrix where. At this stage, all samples display approximately the same wear rate in the range \((0.80-0.99) \times 10^{-4} \text{ g·m}^{-1}\). The global higher wear resistance is obtained for the NC4 sample that is in concordance with the level of corresponding average microhardness. Global values characterizing the wear behavior are given in Table IV.

IV. CONCLUSION

Based on the obtained experimental results, the following conclusions could be drawn:

1. Prescribed heat treatment parameters (i.e. austenitising temperature: 1050°C; holding time: 15 min; medium quench: oil bath and both tempering temperature: 500 and 600°C for 2 h) allowed to:
   - Obtain an optimum dissolution of the primary alloy carbides present in the annealed state.
   - Achieve a reliable tempered martensitic microstructure (without bainite) in which are embedded complex carbides type-M23C6 (M is chromium mainly which include both molybdenum and vanadium dissolved in them) without any retained austenite content. These features yield a reached satisfactory hardness value of 53 HRC.

2. Chemistry of the material showed that:
   - According to the obtained results, in conjunction with those provided by the literature, the lower silicon content (~0.55%) might have a favorable effect in tempering, as it contributes to a possible use of the tool steel in higher in-service temperature.
   - The lower vanadium content (~0.35%) supplied a positive effect on the primary grain size and remained enough to prevent grain coarsening and to avoid the formation of undesirable indissolved carbides that can subsist along prior austenite grain boundaries throughout the thermal processing of the material.
   - The presence of the high-level carbon content (~0.52%) and the chosen cooling medium (oil bath) could give unsatisfactory results, leading to the formation of cracks. As a remedy, a martempering process is most advisable.

3. The benefits of prescribed subsequent salt bath nitrocarburizing performed at 580°C for 2, 4, 6 and 8 h treatment led to some conclusions, as below:
   - Based on the presence of alloying elements, various tested samples disclosed a relative thinner compound layer, lying in the range (7.50-13.54) μm and comprising dominant ε-phase (i.e. NC4 sample) that could promote resistance to spalling as well as wear resistance, respectively. Corresponding diffusion zone depths were respectively 60.50, 68.60, 102.70 and 127.50 μm, which could be considered as satisfactory.
   - Relevant hardness values at the surface (1010-1200) HV0.05 are achieved whereas those corresponding to the core (520-530) HV0.05 remained approximately unchanged with regard to the prior treatments, featuring a better load support of the base material (reliable toughness).
   - A nitrocarburized material for 4h showed the best wear behavior that is concomitant with its corresponding hardness level of 1200 HV. This feature could be attributed to the properties of both diffusion zone, including carbonitrides and hard precipitates and compound layer, consisting predominantly of monophase epsilon nitrides.

4. Summarizing, the implementation of the combination of a prescribed preliminary heat treatments with subsequent salt bath nitrocarburizing in a single production process, as outlined in this paper, in addition to research information available from other sources, allowed suggesting that newly as-studied tool steel could be successfully employed for different applications.

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