Chemical and Phase Composition of Vacuum Oxy-nitrocarburized Pure Iron, Carbon and Low Alloyed Steels

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Abstract: In this study different substrates are saturated in vacuum with N, C and O in NH\(_3\) and CO\(_2\) gas mixture in order to increase their surfaces’ properties. The carbon amount (CO\(_2\)) in the nitriding atmosphere (NH\(_3\)) was 10 vol. % at a pressure of 8.10\(^4\) Pa and the process time was 7 h. The pure iron is used as a referent substrate in order to reveal the process potentialities while the other ones are commonly used grades for machine parts manufacturing that undergo abrasive and adhesive wear. The influence of the structural difference on the chemical composition, X-ray diffraction pattern and hardness of the oxy-nitrocarburized specimens were performed.

Key-Words: oxy-nitrocarburizing; pure iron; steel; chemical, phase composition; hardness.

1 Introduction

There are different gaseous ferritic nitrocarburizing methods among which are the low pressure processes in NH\(_3\) + CO\(_2\) mixture atmosphere. During gas oxy-nitrocarburizing at subcritical temperature, two-part carbo-nitride layer – compound and diffusion one, is formed. The resistance against corrosion, abrasive and adhesive wear is dependent on the structure and relative hardness of the compound layer. The CO\(_2\) containing nitriding gas phase has a comparatively high oxygen potential and the oxygen atoms accelerate the Fe\(_{2.3}(N,C)\) formation [1], especially at low pressure conditions. The main disadvantage of all gas nitriding and nitrocarburizing processes is the difficult in the control over layers’ phase structure. So, the aim of this study is to determinate the structural and phase differences of vacuum oxy-nitrocarburized layers formed on pure iron substrate and steel samples in NH\(_3\) and CO\(_2\) containing gas phase.

2 Experimental details

Four samples - pure iron, AISI 1045 (C45), AISI 5140 (41Cr4), AISI 4140 (42CrMo4) with average size Ø20x10mm and chemical composition (“SPECTRON” quantometer) listed in Table 1, are used as substrates for oxy-nitrocarburizing (ONC). Before the ONC, the steel samples were quenched and high-temperature tempered (620 - 650°C), polished, lapped and degreased. The vacuum ONC was carried out in industrial equipment for 7 hours at 570°C in NH\(_3\) and CO\(_2\) atmosphere. The pressure in the vacuum chamber has been 8.10\(^4\) Pa for the first 5 hours and 1.10\(^5\) Pa during the last 2 hours [2]. The cooling off has been carried in the NH\(_3\) atmosphere till 400°C and after that in N\(_2\). The surface hardness is measured by a mobile ‘Krautkramer’ Vickers tester (before and after the ONC) under a load of 1 kg. The microstructure was etched by 4%-solution of HNO\(_3\) in ethyl alcohol (Nital) and Murakami reagent. The structural characteristics before and after surface modification were investigated using Olympus BX41M optical microscopy. X-ray diffractometer URD-6 using FeK\(\alpha\) radiation was used to determine the phase composition. The GDOES analysis was made with “Leco instruments” apparatus GDS-750 QDP.

3 Results and Discussions

3.1 Chemical and phase composition

Fig. 1 displays the chemical elements distribution of the ONC pure Fe (fig. 1a) and carbon steel (fig. 1b) respectively. It is known that as the nitrogen concentration in the gas mixture is increased, the relative amount of \(\varepsilon\)-phase in the compound layer mounted and that of \(\gamma'\)-phase decreases. In comparison of \(\gamma'\)-phase, \(\varepsilon\)-Fe\(_{2.3}(N,C)\)
has much wider solubility range of nitrogen, which enable to produce a steeper concentration gradient as it is shown in both samples nitrogen distribution. This fact facilitates the faster growth of the ε-phase.

Table 1. Pure iron and examined steels chemical composition (wt %).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Fe</td>
<td>0.002</td>
<td>0.01</td>
<td>0.05</td>
<td>0.014</td>
<td>0.002</td>
<td>0.015</td>
<td>0.009</td>
<td>0.004</td>
<td>Bal</td>
</tr>
<tr>
<td>AISI 1045</td>
<td>0.42</td>
<td>0.26</td>
<td>0.83</td>
<td>0.095</td>
<td>0.009</td>
<td>0.040</td>
<td>0.025</td>
<td>0.020</td>
<td>Bal</td>
</tr>
<tr>
<td>AISI 5140</td>
<td>0.39</td>
<td>0.30</td>
<td>0.67</td>
<td>1.03</td>
<td>0.016</td>
<td>0.132</td>
<td>0.010</td>
<td>0.011</td>
<td>Bal</td>
</tr>
<tr>
<td>AISI 4140</td>
<td>0.38</td>
<td>0.29</td>
<td>0.69</td>
<td>1.06</td>
<td>0.18</td>
<td>0.185</td>
<td>0.012</td>
<td>0.020</td>
<td>Bal</td>
</tr>
</tbody>
</table>

According to the fig.1a, the concentration of nitrogen, carbon and iron on the surface corresponds to ε-Fe$_2$3(N,C) phase composition at the processing temperature. A typical distribution behavior in iron, nitrogen and oxygen pure Fe curves is observed. The lack of sharp concentration stages in all elements’ profiles is due to the roughness of the surface (Ra ~ 11-12μm), non-perpendicular saturation in depth of the substrate as well as differences in the thickness of the compound layer. The vacuum sputtering process during GDOES analysis is made perpendicularly to the surface. Near to the compound layer/α-solid solution boundary the phases’ proportion slightly changes because of the “teeth-like” ending of the upper layer as it is shown on fig. 2b. It could be seen on the microstructure image that the diffusion frontage penetrates faster through the grains’ boundaries and certain grains. Some authors thought that Fe$_4$N phase grows up faster in {210} orientated grains in <100> direction [3]. So, the area at the interface of the base metal and the compound layer where predominantly γ’-phase is located, has a very “uneven” structure for this type of analysis. That’s why there is not a sharp transition from the compound to diffusion layer in the nitrogen concentration.

![Fig. 1. GDOES and X-ray pattern of the oxy-nitrocarburized samples:](image-url)
According to the ternary Fe-C-N diagram [4] from the surface area down to the end of the pure iron compound layer there are ε- and γ'-carbonitride phases present in different proportions. The ε-Fe\textsubscript{2-3}(N,C) predominates over the γ'-phase in the outermost area of the layer. So, there is a reducing gradient correlation between ε/γ'-phases in the compound layer depth. Most authors associate the predominant ε-phase presence and a smaller amount of γ'-phase in the compound layer with a better wear resistance. This fact corresponds to the X-ray analysis results of the sample (fig. 1c).

As it could be seen, the relative amount of ε-phase prevail over the γ'-one. There are also two small α-peaks shown through the substrate.

The carbon enrichment in the pure Fe, which comes only from the gas phase carbon source, reaches up depth about 6 μm. In the diffusion layer the carbon concentration decreases because of its low ferrite solubility. The slight increase in its concentration at about 2.5 μm is probably due to the roughness of the surface and different diffusion rate of the nascent elements in the compound layer phases as their proportion changes.

![Fig. 2 Pure iron microstructure image: a) compound and diffusion layer (2000x), etched with nital and Murakami (2000x); b) compound and diffusion layer (500x) etched with nital.](image)

An interesting fact in the AISI 1045 steel GDOES analysis (fig. 1b) is the initial decrease in the iron concentration together with the increase in the oxygen one. There is an excess nitrogen concentration on the surface (over 50% at the carbon steel surface), resulting in pre-saturation of the ε-phase. During the cooling stage of the process, the temperature lowering increases the nitrogen potential and additional pre-saturation of the ε-phase is observed. According to some authors, free nitrogen atoms or molecules are exerted when the surface nitrogen concentration exceeds 26 at. % [5]. The Fe-nitrides have high values of formation free Gibbs energies as opposed to the stable Fe-oxides. So, ε and γ' are unstable phases especially in presence of carbon in the gas atmosphere and they could easily dissociate following the reaction:

\[ 2\text{Fe}_{\text{N\,d}} + N_2 \rightarrow 6/8\text{Fe} + N_2. \]

The nitrogen recombinates enhances surface microporosity [6]. That fact corresponds to the elements fluctuation near to the surface of the carbon steel. Unlike, there is not such a fluctuating behavior of the elements at the pure iron surface probably because of the lower (approximately 40%) nitrogen concentration.

In the presence of CO\textsubscript{2} in the atmosphere, the homogeneous water-gas reaction could take place:

\[ \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \]

The water vapor has a considerably lower partial oxygen pressure as compared to that of the oxygen molecule. The industrial cooling N\textsubscript{2} gas always contains oxygen impurities with partial pressure about 10^-5-10^-6 bar [7]. Then, according to [8], the released iron atoms could be oxidized as followed:

\[ 3\text{Fe} + 4\text{H}_2\text{O} \leftrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2. \]

Therefore, an up going iron diffusion process driven by the higher surface oxygen potential could also be the reason for microporous formations to occur when a high surface nitrogen concentration is observed. The presence of oxidized micropores causes a lowering in surface iron concentration, discerned in GDOES analysis while the oxide layers are very thin and could not be X-ray determined (fig. 1d). The oxides occur in the open coalesce channels connections with the outer oxidative atmosphere and inside the compound layer micropores [9]. The surface polishing
operation before GDOES analysis removes the upper located oxides except that present in the micro pores’ walls. These oxides appear in the elements distribution profile. It is known that the oxidized micropores improve the corrosion resistance and tribological properties, possibly by functioning as micro-reservoirs for lubricants.

The GDOES analysis shows that the compound layer at the carbon steel surface has a higher thickness (over 15 μm) unlike that in the pure Fe (about 10 μm). The defined phase composition (fig. 1b,d) do not substantially differ from the pure iron one. A possible explanation of the difference in the compound layer depth is the interference of CO₂ gas molecule with the cementite from the substrate:

\[ 4\text{Fe}_3\text{C} + 3\text{NH}_3 + \text{CO}_2 \leftrightarrow 3\text{Fe}_4\text{N} + 2\text{CO} + 2\text{H}_2 \]

The CO₂ presence in the gas mixture is one reason for the ε-phase prevalence in the phase structure (fig. 1d). Another one is the facilitated conversion of the substrate Fe₃C into ε-Fe₂₋₃(N,C) over the influence of nitrogen in the steel [10]. Therefore, the ε-phase nucleation occurs earlier as compared to that in the pure Fe sample and the pre-saturation with nitrogen of the steel Fe₂₋₃(C,N) phase is higher.

It is known that with the increase in carbon and alloying elements content, the rate of diffusion decreases thus resulting in shallower depths of nitrogen and carbon penetration. This effect is shown in AISI 5140 and AISI 4140 steels chemical distribution profiles (fig. 3). As opposed to the other two sample, the α-peaks shown through the substrates have a higher intensity than the carbonitride phases’ intensities (fig. 3c,d). The predominant phases in both samples are also ε-Fe₂₋₃(N,C) ones.

![GDOES and X-ray pattern of the oxy-nitrocarburized samples](image)

**Fig. 3.** GDOES and X-ray pattern of the oxy-nitrocarburized samples: a) elements distribution in depth of AISI 5140 steel; b) elements distribution in depth of AISI 4140 steel; c) X-ray pattern of AISI 5140 steel; d) X-ray pattern of AISI 4140 steel.

At both low alloyed steel surfaces porous structures similar to that at the carbon steel surface are present. The part of the porous area in AISI 4140 steel compound layer is greater than that in the carbon steel unlike the reported in [11]. The nitrogen content falls down sharply and produces a
steeper concentration gradient especially in the AISI 4140 steel. In this sample the ε-phase contains less nitrogen because the nitride precipitation reduces the α-solid solution nitrogen content and the content of nitride-forming alloying elements. The chromium content is slightly increased at the porous side of the compound layer where the oxygen potential is greater. The low process temperature does not substantially activate the chromium up going diffusion. Nevertheless, considerable carbon enrichment at the compound/diffusion layer boundary is observed on fig. 3b. There is such an increase in the carbon content in the AISI 5140 steel but the latter is not so figurative. As a small atom, the carbon diffuses within the substrate at a relatively low temperature (about 200°C). Over the influence of the surface nitrogen enrichment, the chromium movement towards the surface pulls upwards the substrate carbon. The opposite carbon diffusion - downwards the surface and upwards the substrate could be the reason for the observed carbon heaping. Additional researches should be made to reveal the nature for the observed carbon enrichment.

3.2. Hardness measurements
Table 1 presents the hardness values measured after the thermal treatment and after the ONC process. Regarding the load of 1 kg and the samples compound layer thickness, the values measured after ONC perform an average hardness value of the compound and diffusion layers. The hardness of the diffusion layer should be associated with the pre-saturation of the α-solution, nitrides’ precipitation, compressive residual stress [12,13] and the initial hardness of the substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure Fe</th>
<th>AISI 1045</th>
<th>AISI 5140</th>
<th>AISI 4140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before ONC (HV)</td>
<td>110</td>
<td>255</td>
<td>295</td>
<td>290</td>
</tr>
<tr>
<td>After ONC and polishing (HV)</td>
<td>210</td>
<td>550</td>
<td>580</td>
<td>620</td>
</tr>
</tbody>
</table>

As expected, the pure iron hardness increase is the smallest one. Nevertheless, the compound layer hardness of the same sample is HV<sub>0.05</sub> = 505 kgf/mm<sup>2</sup>. Unlike the hardness of the soft Fe-nitrides, the Fe-carbonitrides display enhanced hardness values. The lack of surface oxidized porosity probably contributes to the measured compound layer hardness. The comparatively thick compound layer in the AISI 1045 steel sample as well as the presence of harder chromium nitrides in AISI 5140 steel are the reasons for the exhibited surface hardening. With increasing alloy content of the steel, the diffusion layer is thinner for identical ONC parameters (fig.3 a, b). Nevertheless, with the higher level of the nitride forming elements these steels have a greater hardness (tabl.1). These values may be associated not only with the alloying element nitrides presence, but also with the increase in the carbon content underneath the compound layer.

4. Conclusions
The main conclusions of this study could be summarized as follow:
1. A typical distribution behavior in the iron, nitrogen and oxygen GDOES analysis curves in the pure iron sample is observed at these particular oxy-nitrocarburizing conditions. There are ε- and γ’-carbonitride phases present in iron compound layer but in different proportion. The lowest nitrogen surface concentration is observed at this sample;
2. The lack of sharp concentration stages in all elements’ profiles in the samples is due to the roughness of the surface (R<sub>a</sub> ~ 11-12μm), non-perpendicular saturation in depth of the substrate as well as difference in the thickness of the compound layer;
3. The ε-Fe<sub>2</sub>3(N,C) phase predominates on the outermost area of the compound layer over the γ’-one in all samples;
4. The compound layer at the carbon steel surface has the highest thickness of all samples and the greatest surface nitrogen concentration;
5. In contrast to the pure iron, there are oxidized micropores in all of the treated steel samples related with surface elements fluctuation. The porous parts in AISI 4140 and AISI 5140 steels compound layer are greater than that in the carbon one;
6. The presence of Fe<sub>3</sub>C in the substrates causes earlier ε-phase nucleation as compared with the pure Fe and the Fe<sub>2</sub>3(C,N) nitrogen pre-saturation in them is higher;
7. With the higher level of the nitride forming elements and the increase in the carbon content
underneath the compound layer the alloyed steels display greater hardness values.

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