

Nitretação em aços de baixo carbono utilizando banhos de sais atóxicos

Nitriding in low carbon steels using non-toxic salt baths¹

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Resumo

O objetivo deste artigo é desenvolver um método de nitretação em banhos de sais atóxicos, utilizando nitrato de potássio (KNO_3) e nitrito de sódio ($NaNO_2$), bem como, avaliar a dureza e o aspecto visual da camada superficial de um aço com 0,2% de carbono, vislumbrando uma alternativa que busca redução no impacto ambiental, gerado pelo processo convencional de nitretação em banho de sal, contendo cianeto e cianato. Também, estudou-se meios que reduzam os óxidos não aderentes, gerados durante o processo de nitretação. Os resultados indicam que os sais KNO_3 e $NaNO_2$ atuam na formação de uma camada nitrada, evidenciada pela mudança microestrutural e pelo aumento da dureza da camada, em relação ao material sem tratamento. Porém, dependendo das proporções entre sal atóxico e sal redutor de óxido, tem-se melhor acabamento superficial, o que contribui para o meio ambiente, pois evita a geração de resíduos na base de cianeto e cianato.

Palavras-chave: Aço baixo carbono. Nitretação. Banho de sal atóxico.

Abstract

The objective of this article is to develop a method of nitriding in non-toxic salt baths, using potassium nitrate (KNO_3) and sodium nitrite ($NaNO_2$), as well as to evaluate the hardness and the visual aspect of the surface layer of a steel with 0.2% carbon, seeking for an alternative to reduce the environmental impact caused by the conventional process of nitriding in salt bath containing cyanide and cyanate. It was also studied some means that can reduce the non-adherent oxides generated during the nitriding process. The results indicate that the salts KNO_3 and $NaNO_2$ act in the formation of a nitrated layer, evidenced by a microstructural change and the increase of the layer hardness, in relation to the material without any treatment. However, depending on the proportions between non-toxic salt and oxide-reducing salt, there is a better surface finishing, which contributes to the environment, as it avoids the generation of cyanide and cyanate-based residues.

Keywords: Low carbon steel. Nitriding. Non-toxic salt bath.

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1 Introduction

The task of improving the properties of metallic materials in modern mechanical engineering is closely related to the development of new processes of surface hardening of the produced parts (TSIKH *et al.*, 2011).

Low carbon steels have economic advantages when compared to other materials. Although they are notable for their low cost, good mechanical properties and good conformability, they are susceptible to corrosion. Several methods are available to prevent this phenomenon, (VOURLIAS; PISTOFIDIS; STERGIOUDIS, 2008). Some of these methods are superficial treatments, which are considered the best methods to prevent corrosion, friction and wear (CAI *et al.*, 2012; PENG, 1989; PODGORNİK *et al.*, 2001). For these superficial treatments, there are three basic requirements for coatings: good adhesion, chemical stability as well as high structural and phase stability (GHELLOUDJ *et al.*, 2016; THIELE; LEHNERT, 2017).

Nitriding is a technique of superficial treatment, which proposes the input of nitrogen in the crystalline net of metallic materials, through diffusive processes that depend on time and temperature. Its function is to increase surface hardness, mechanical properties, wear and corrosion resistance. The nitriding methods established include gas nitriding, plasma nitriding, liquid nitriding, and laser nitriding (SHEN; OH; LEE, 2005).

The characteristics of the deposited layers depend on the process parameters, as well as the composition of the process and the alloy to be treated. Nitriding can be performed in liquid, gaseous and plasma states. The liquid process, usually performed in bath of molten salts, requires shorter processing time, is easy to implement, and has wide usage. For salt bath nitriding, mainly cyanides (sodium cyanide or potassium cyanide) and cyanates (sodium cyanate or potassium cyanate) are used. However, it is preferred to have cyanide and/or cyanate free-salt baths due to their lower risk to environmental impact (BALIKCI; YAMAN, 2011).

Studies on the use of non-toxic salts in the nitriding process indicate satisfactory results, when compared to salt baths containing cyanides. Among the properties analyzed, most of them compare the superficial hardness in relation to the conventional process and also mechanical properties (BALIKCI; YAMAN, 2011; FUNATANI, 2004; LEE *et al.*, 2010; SHEN; OH; LEE, 2005). The salt used, the parameters of time and temperature are described, but there is a lack of information about

the visual aspect of the layer and the composition of the baths.

Thus, the aim of this article is both to develop a method of nitriding in non-toxic salt baths using potassium nitrate (KNO_3) and sodium nitrite (NaNO_2) to evaluate the visual aspect of the layer and the surface hardness of a low carbon steel designated by the standard NBR 87 NM (ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, 2000) as 1020 and to seek for an alternative to reduce the environmental impact caused by the conventional process of salt bath nitriding containing cyanide and cyanate. Some means that can reduce non-adherent oxides generated during the nitriding process (Scale) were also studied.

The steps needed for the development of this study went through the preparation of samples, the nitriding of them in non-toxic salt baths, the evaluation of the layer generated by optical microscopy and superficial hardness, and, finally, the addition of additives to reduce the surface oxides that were generated.

2 Development

2.1 Theoretical framework

In 1913, the world patent of steel nitriding and cast iron was used for the first time and in 1924, gas nitriding technology was introduced in industries. Some years later, liquid nitriding (also known as salt bath nitriding technology) was developed and applied in the industry. From that moment on, both nitriding techniques were developed quickly and played a dominant function in the nitriding of metal parts. Nonetheless, in the 1960s, the application of gas and liquid nitriding was considerably reduced. The biggest disadvantage for gas nitriding is that it requires high temperatures around 650-1000 °C, as well as a long nitriding process time compared to other nitriding processes as reported in the literature. For liquid nitriding, however, the main disadvantage is the use of toxic cyanide salts (LIU *et al.*, 2018).

Although the methods above are well established, some of them have disadvantages from the engineering point of view, for example, they may require the use of very complex and/or high cost appliances. On the other hand, nitriding by means of liquid salts containing cyanide and cyanate is one of the nitriding methods most widely applied to steel parts. In fact, this process is known as nitrocarbocation, since the environment of molten salt contains carbon and nitrogen, and the two elements generally

diffuse on the surface of the steel parts simultaneously. This aspect complicates the nitriding process, because the carbon spreads toward the steel core and a carbon-rich layer accumulates before the nitride reaction front. As far as we know, until this present day, any nitriding process for steel without simultaneous carbonation was performed with salt baths (GHELLOUDJ *et al.*, 2016; SHEN; OH; LEE, 2005).

Nitriding in molten salts baths require shorter processing time and are easy to implement, with wide application in comparison to other nitriding processes. This process basically consists of using cyanide (sodium cyanide or potassium cyanide) and cyanates (sodium cyanate or potassium cyanate). However, cyanide-free salt baths are preferred due to their lower environmental impact (BALIKCI; YAMAN, 2011).

Cyanide is a fast-acting poison because it associates with enzymes containing iron, necessary for cells to use oxygen and, as a result, tissues are unable to absorb oxygen from the blood (READE *et al.*, 2012). In the absence of first aid, the inhalation, ingestion or absorption through the skin of the gas, can be fatal in a few minutes by poisoning (GOSHMAN, 1985). Part of the cyanide can be altered to thiocyanate, which is less harmful and is excreted from the body by the urine. It can also associate with hydroxocobalamin to form vitamin B12. A small amount of cyanide in the body can be converted into carbon dioxide, which is expelled from the body by breathing. Most of the cyanide and its products are eliminated from the body in the first 24 hours after the exposure (WORLD HEALTH ORGANIZATION, 1998).

Cyanide is one of the fastest-acting poisons known and is responsible for many suicidal and homicidal deaths. Cyanide can come in many ways. The most common ones are hydrogen cyanide (HCN) and cyanide salts (potassium cyanide, sodium cyanide, calcium cyanide), which can combine with acid to release the HCN. Water sources can be contaminated with cyanide by industrial effluents, by the migration of cyanide from landfills and, to a lesser extent, by the draining of salts containing cyanide directly to the surface. The largest sources of cyanide in the water are discharges from organic chemical industries, iron and steel mills and wastewater treatment worksites. A survey conducted by the United States Environmental Protection Agency (EPA) in 1978 showed that about 7% of the samples collected had cyanide concentrations greater than 10 parts per billion (ppb). (The expected standard of drinking water to be proposed by the EPA in 1990 is

200 ppb.) (HUZAR; GEORGE; CROSS, 2013).

Virtually, any substance containing carbon and nitrogen can release cyanide when burnt under certain conditions. HCN is released during pyrolysis of synthetic polymers containing nitrocellulose, acrylonitrile or urea-formaldehyde. Many common textiles, foam and plastic materials at home can be sources of HCN in a fire event. Some natural products, such as silk and wool, can also release cyanide when burnt (HUZAR; GEORGE; CROSS, 2013).

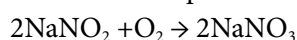
The proposal to develop nitriding with nitrate is considered a promising method for the input of nitrogen in iron and steel, although the surface oxidation cannot be avoided. The oxidation of the surface can cause not only a slight loss of steel, but also a reduction in the rate of nitriding, because of the surface layer of oxide that hinders the nitrogen sources that reach the steel (LEE *et al.*, 2010).

The use of potassium nitrate (KNO₃) was introduced for the first time in 2005 (LEE *et al.*, 2010; SHEN; OH; LEE, 2005). The nitrogen source in nitriding was attributed to nitrous oxide (NO) and nitrogen dioxide (NO₂) generated from the decomposition of KNO₃ at temperatures above 500 °C. It was suggested that NO and NO₂, as well as the nitrogen generated from the decomposition of KNO₃, could participate in nitriding and oxidation reactions. The thermal decomposition behavior of sodium nitrite (NaNO₂) and sodium nitrate (NaNO₃) is similar to potassium nitrate KNO₃ (LEE *et al.*, 2010; SHEN; OH; LEE, 2005).

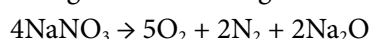
According to Lee *et al.* (2010) and Shen, Oh and Lee (2005), the perceptible thermal decomposition of sodium nitrite occurs like this:



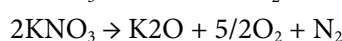
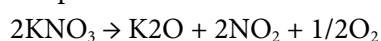
If oxygen is present, nitrite may oxidize to nitrate at similar temperatures:



Oxygen can be present in the air inlet or in the decomposition of nitrates at high temperatures. Sodium nitrate begins to decompose above 500 °C, according to the following reactions:



For potassium nitrate:



In both salts there is the presence of nitrogen (N), oxygen (O) but the presence of cyanates (carbon + nitrogen or carbon + nitrogen + oxygen, respectively) is not found. However, as a negative point, there is the presence of free oxygen, causing oxidation on

the surface of the sample that will be in this salt bath (LEE *et al.*, 2010; SHEN; OH; LEE, 2005).

To avoid the superficial oxidation of the sample Lee *et al* added sodium chloride (NaCl) and potassium chloride (KCl) to the non-toxic salts bath. In addition to avoiding the oxidation of the work piece surface, the use of sodium chloride accelerates the diffusion process, because the surface oxidation hinders the nitrogen diffusion process (LEE *et al.*, 2010).

Although there are some data published on the use of non-toxic salts and additives for nitriding, information on proportions and visual aspect of the obtained layer are not clearly exposed, and the proposal of this article complements these other studies.

2.2 Materials and methods

The material used for conducting the experiments is the compound of the low carbon alloy

1020, according to the designation NBR NM 87 (ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, 2000), with approximate dimensions of Ø19x10 mm, and with certificate of composition Chemistry presented in table 1 below:

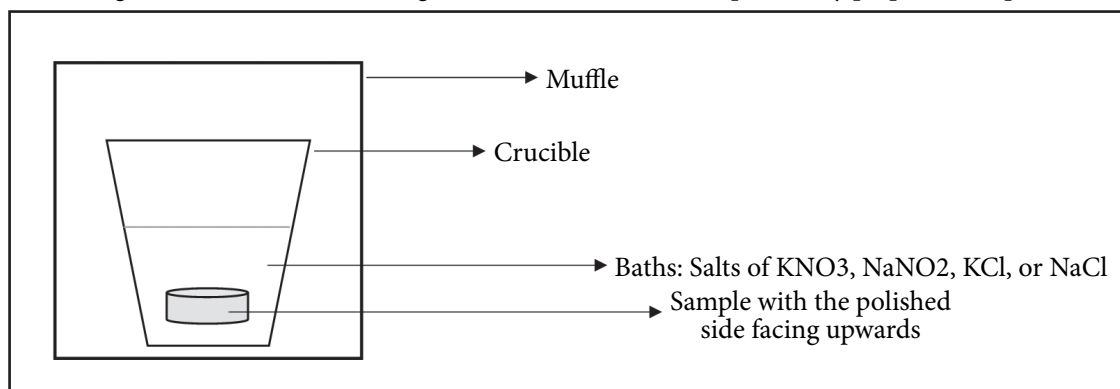
Table 1- Chemical composition of the sample used

C	Si	Mn	P	S
0.220	0.170	0.540	0.022	0.013

Source: The authors (2018).

The methodology used was described by Lee *et al.* (2010) and Shen, Oh and Lee (2005) who were the precursors of the treatment in non-toxic salts. The parameterization is presented in figure 1. An uncontrolled atmosphere muffle furnace with temperature of 650 °C was used for 3 hours.

Figure 1 – Process of nitriding in non-toxic salts baths of previously prepared samples



Source: The authors (2018).

Cylindrical metallic samples of the 1020 steel, with surface area for analysis of approximately 3 cm², were previously sanded with sandpaper, starting with the sandpaper of grain size from 120 up to 1200; after that, the samples were polished and cleaned up. In a beaker was added a solution consisting of water and detergent, in which the samples were immersed. The beaker was placed in the ultrasound equipment for 20 minutes without any temperature increase. After these 20 minutes, the samples were taken out from the beaker (with water and detergent solution) and, then, transferred to a beaker with acetone, in which, again, it was subjected to ultrasonic bath for 20 minutes.

In a porcelain crucible, the clean samples were placed together with sufficient amounts of salts to completely cover the samples. After 3 hours, the samples were taken from the crucible and cooled in distilled water at room temperature.

The visual aspects of the layers obtained with non-toxic salts (used as nitrogen source in the pure condition) were analyzed in a stereoscopic microscope.

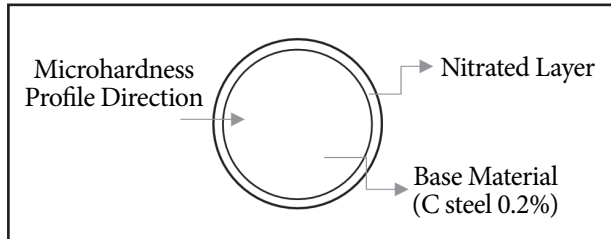
As for the scheme on figure 2, the samples were transversely cut and also sanded, starting with sandpaper of grain size from 120 up to 1200. After that, they were polished and embedded in acrylic resin.

To reveal the microstructure, a 10% Nital chemical attack was used. The microstructural analysis was performed in an optical microscope, where mainly the layer obtained by nitrogen diffusion on the sample surface was observed.

The microhardness analysis was performed based on ASTM E92 and ASTM E384 with the use of a microdurometer, Vickers indenter and load 0,245N. The indentations departed from the end (nitrided layer) towards the center, with spacing of

0.04 mm between each indentation. The analysis was ceased when the hardness reached constant values.

Figure 2 – Top view schematic figure of nitrided layers indicating direction of Vickers microhardness profile



Source: The authors (2018).

The sense of analysis is presented in figure 2.

In addition to the salts that act as a source of nitrogen to obtain the iron nitride, the mixture of chloride salts (sodium chloride and potassium chloride) was tested to decrease the oxidation of the layer obtained according to the following proportions

Table 2 - Proportion of salts used as additives to decrease the formation of non-adherent superficial O-S in Kulikov (2001)

Experimental condition	Non-toxic Salt	Oxide reducer Salt
1	75% NaNO ₂	25% NaCl
2	75% NaNO ₂	25% KCl
3	75% KNO ₃	25% NaCl
4	75% KNO ₃	25% KCl

Source: The authors (2018).

presented on table 2 below (KULIKOV, 2001):

Also, as a form of study and verification of the results, some parameters were altered, maintaining only the non-toxic salt consisting of NaNO₂ and varying the proportion of the oxidation reducer salt,

Table 3- proposed variation in the proportion of salts used as additives to decrease the formation of non-adherent superficial oxides

Experimental condition	Non-toxic Salt	Oxide reducer Salt
5	50% NaNO ₂	50% NaCl
6	50% NaNO ₂	50% KCl
7	60% NaNO ₂	40% KCl
8	70% NaNO ₂	30% KCl
9	50% NaNO ₂	30% KCl + 20% NaCl

Source: The authors (2018).

shown on table 3 below:

According to Chiaverini (2005), a typical commercial bath for liquid nitriding consists of a mixture of 60% to 70% of sodium salts and 30% to 40% of potassium salts. This experimental condition was also tested with the addition of the oxide reducer

Table 4 -Parameters for the use of O-oxide reducing salts

Experimental condition	Non-toxic Salt	Oxide reducer Salt
10	70% NaNO ₂ + 30% KNO ₃	-
11	50% NaNO ₂ + 30% KNO ₃	20% NaCl

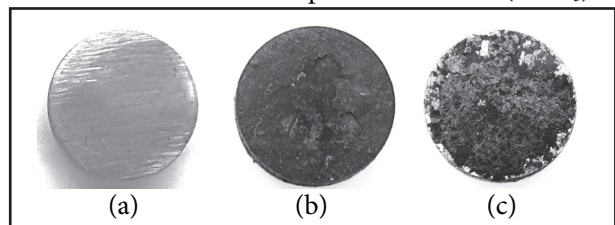
Source: The authors (2018).

salt, as shown on table 4:

2.3 Results

The images presented in figure 3 show the samples after the non-toxic salt bath. As we can observe, there is a large presence of oxides (scale) generated on the surface of the parts, where we can, qualitatively, verify the smallest formation in the sample

Figure 3 – (a) non-nitrided sample; (b) sample nitrided in salt bath with sodium nitrite (NaNO₂); (c) sample nitrided in salt bath with potassium nitrate (KNO₃)

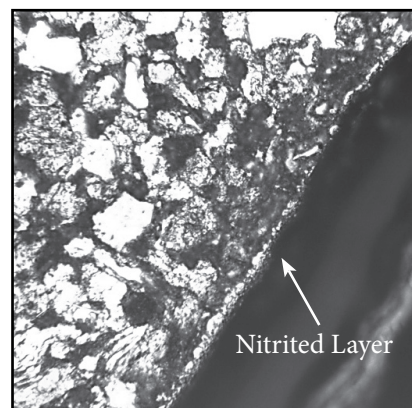


Source: The authors (2018).

nitrided in salt bath of KNO₃ when compared to the NaNO₂ salt bath.

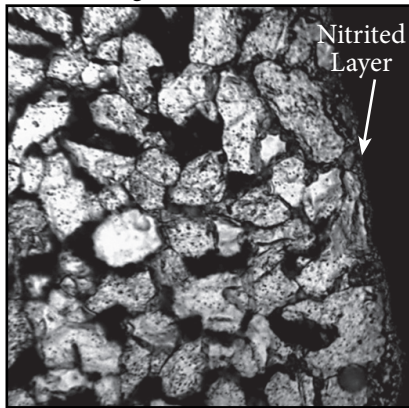
The metallographic analysis contained in figure 4 shows the metal matrix formed by ferrite (light phase) and perlite (dark phase), and the nitrided layer with KNO₃ is evidenced on the external surface as a linear light phase color. In figure 5, the layer obtained by nitriding with NaNO₂ is presented, which

Figure 4 - Photomicrography of the layer obtained by the bath in salt of potassium nitrate (KNO₃) enlarged in 400 times



Source: The authors (2018).

Figure 5 – Photomicrography of the layer obtained by the bath in salt of sodium nitrite (NaNO_2) enlarged in 400 times



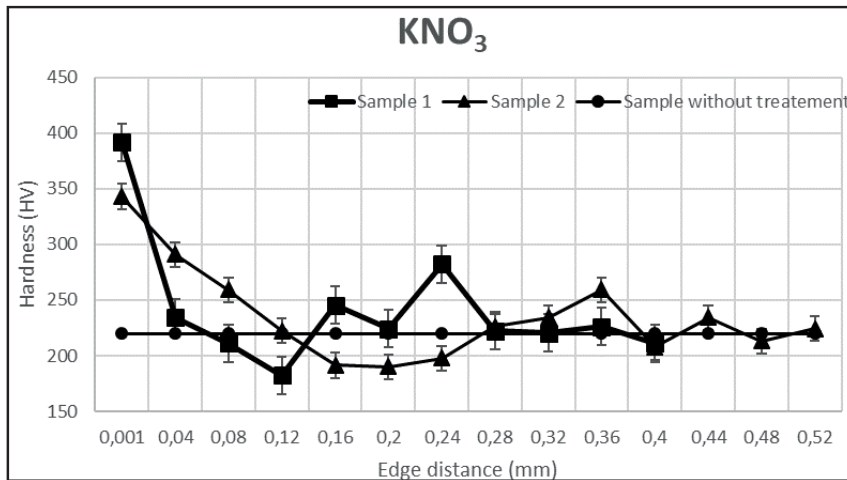
Source: The authors (2018).

also presents matrix composed of ferrite and perlite, and the nitrided layer is not so evident.

The hardness obtained by the profile along the nitrided layer is presented in figure 6 and figure 7. The microstructural analysis showed that the nitrided layer was more evident in the salt bath of KNO_3 . The increase in hardness in the regions near the external surface of the samples occurred in both nitrided layers, however, the KNO_3 also showed to be more significant, where there was a gain of 181 HV of hardness, a fact also presented in the works of Lee *et al.* (2010) and Shen, Oh and Lee (2005), proving the efficiency of the process in non-toxic salt bath.

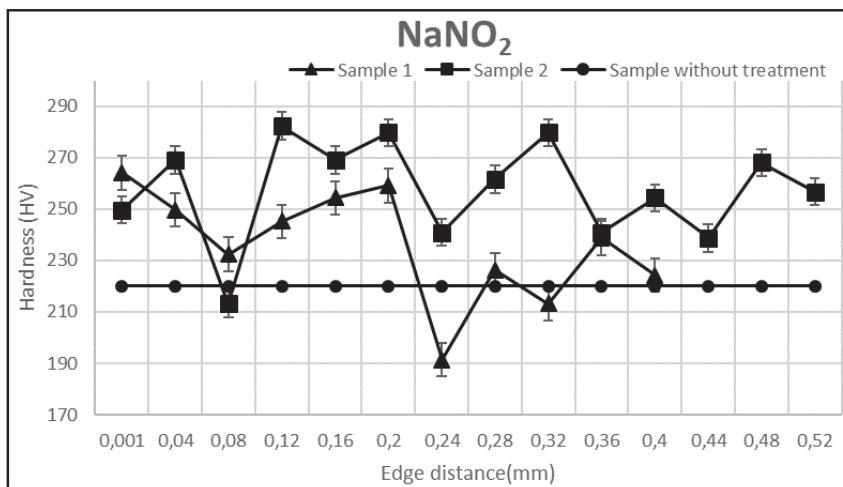
The values presented in figure 6 and figure 7 were statistically validated by the analysis of

Figure 6 – Vickers hardness distribution of steel 1020 nitrided in KNO_3 at 650 °C for 3 h



Source: The authors (2018).

Figure 7 – Vickers hardness distribution of steel 1020 nitrided in NaNO_2 bath to 650 °C for 3 h



Source: The authors (2018).

Table 5 - Analysis of variance for samples in KNO₃ at 650 °C for 3h

Group	Count	Sum	Average	Variance		
Column 1	11	2652.6	241.1	3102.4		
Column 2	14	3293.5	235.2	1757.7		
ANOVA						
Variation Source	Sq	Gl	Mq	F	P-Value	Critical F
Between groups	214.1	1	214.1	0.1	0.8	4.3
Within the groups	53873.8	23	2342.3			
Total	54087.9	24				

Source: The authors (2018).

Table 6 - Analysis of variance for samples in NaNO₂ bath at 650 °C per 3h

Group	Count	Sum	Average	Variance		
Column 1	11	2652.6	241.1	3102.4		
Column 2	14	3293.5	235.2	1757.7		
ANOVA						
Variation Source	Sq	Gl	Mq	F	P-Value	Critical F
Between groups	214.1	1	214.1	0.1	0.8	4.3
Within the groups	53873.8	23	2342.3			
Total	54087.9	24				

Source: The authors (2018).

variance with 95% reliability performed in Excel software. This analysis is presented on table 5 and table 6.

This analysis proves that the values found for both samples tested in potassium nitrate bath are statistically equal, in which the calculated F is less than the F tabulated. Nonetheless, the values found for the samples tested in sodium nitrite bath are different when compared to each other, because the calculated F is greater than the F-table. These data attest more efficiency in the process of nitriding in non-toxic salt baths using potassium nitrate.

After the nitrating process with the salts of potassium nitrate and sodium nitrite, as well as the mixtures with sodium chloride and potassium chloride, the visual aspects of nitrated surfaces presented dark colored layers, as observed in the images in figure 8.

The presence of "scales" in the images in figure 8 shows the exposure of samples to oxygen. This fact may be attributed to the presence of oxygen in the molecular formula of salts KNO₃ and NaNO₂, as well as the oxidation atmosphere of the furnace.

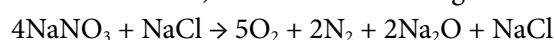
The addition of KCl salt in both mixtures

produced an improvement in the surface finish of the samples, reducing the formation of superficial oxides (scales), when compared to KNO₃ and NaNO₂ salt baths isolated (in pure condition).

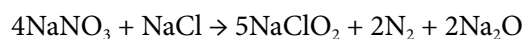
An improvement can also be observed in the superficial layer for the addition of NaCl salt, where there is the presence of oxides in smaller quantities, when compared to the use of salts KNO₃ and NaNO₂, (in pure condition).

This is because:

- The addition of NaCl to sodium nitrate (oxidized sodium nitrite) leads to the following reaction:



With the temperature of 650 °C, the reaction evolves to:

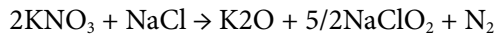


The oxygen will bind with the sodium chloride, reducing the oxidation of the part, and keeping the nitrogen free for the diffusion process.

- With this, the addition of NaCl to potassium nitrate may result in:

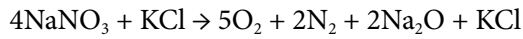


And the temperature increase to 650 °C comes to:



In this case, oxygen will also bind with sodium chloride, reducing the oxidation of the part, and keeping the nitrogen free for the diffusion process. In both cases there is the formation of sodium chlorite.

- The addition of KCl to sodium nitrate (oxidized sodium nitrite) leads to the following reaction:



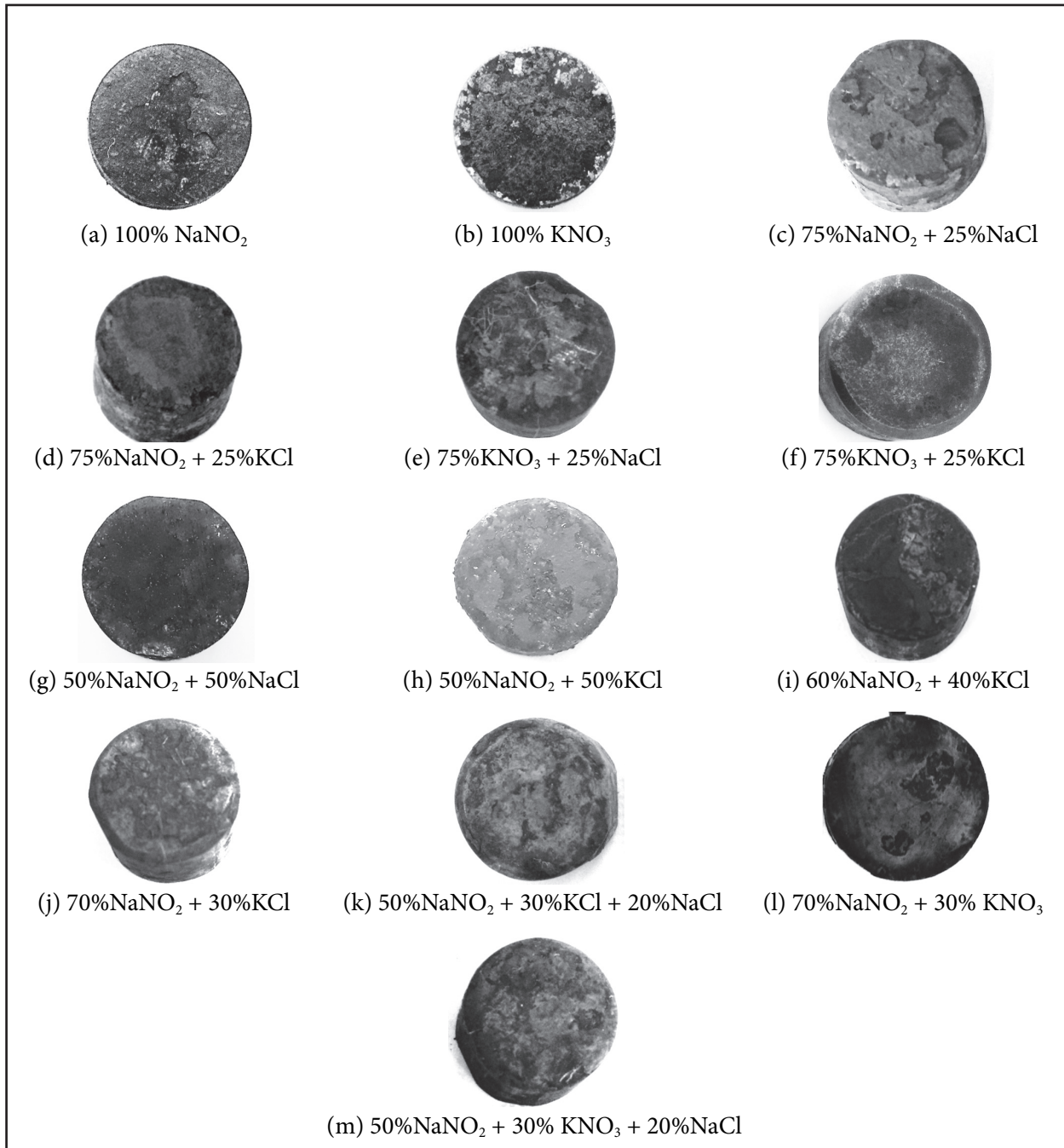
With the temperature of 650 °C, the reaction evolves to:



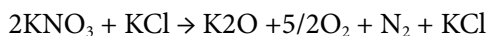
The oxygen will bind with potassium chloride, reducing the oxidation of the part, and keeping the nitrogen free for the diffusion process.

- With this, the KCl addition in potassium nitrate may result in:

Figure 8 – Images of nitrated surfaces



Source: The authors (2018).



With the temperature of 650 °C it will reach:



In this case, oxygen will also bind with potassium chloride, reducing the oxidation of the part, and keeping the nitrogen free for the diffusion process. In both cases there is the formation of potassium chlorate.

It is worth noting that in the process of nitriding in salts baths, used at industrial level, also occurs the formation of oxides on the surface of the nitrated work piece, with the need to undergo subsequent processes of superficial finishing (sanding or blasting, for instance).

3 Conclusion

The results indicate that the salts KNO_3 and NaNO_2 act in the formation of a nitrated layer, evidenced by the microstructural change and increase of the hardness of the superficial layer in relation to the untreated material, but surface oxide formation was obtained after treatment.

Using the non-toxic salt with the reduction of oxide, an improvement in the surface finish was observed, reducing the formation of superficial oxides (scales), by increasing the proportion of the reducing salt.

Thus, it is possible to conclude that the use of non-toxic salts allows us to produce layers of greater hardness when compared to the sample without treatment, being up to 40% for the salt KNO_3 , and up to 18% for NaNO_2 salt. Associated with oxide reducer salts it is possible to improve the visual aspects of the samples, reducing the scales generated by the treatment.

Besides improving the surface properties (reduction in oxide formation) of the low carbon steel, the use of the salts KNO_3 and NaNO_2 also contributes to the environment, as it avoids the formation of cyanide and cyanate based residues, which have high toxicity levels.

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