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Influence of chromium on the diffusion kinetics of nitrogen and carbon at low temperature

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Abstract

Our task in this work was to follow the technology of implementation of liquid nitriding and to carry out salt bath nitrocarburizing treatments on pure iron and binary iron-chromium alloys in order to highlight the influence of chromium on the kinetics of diffusion of nitrogen and carbon in the ferritic phase. While achieving nitrocarburizing iron-chromium binary alloys. The objective was to follow the evolution of the microscopic properties of the layers obtained after nitrocarburizing treatment and to study the microstructural changes and the microhardness as a function of the chromium content chosen. All the results obtained have allowed us to observe that the kinetics of nitrogen diffusion depend strongly on the chromium content. The diffusion depth of the nitrogen and the thickness of the white layer are lower than the chromium content is high.

Keywords: Kinetic, Thickness, Diffusion, Chromium, Nitrocarburizing

1. Introduction

Surface engineering is the technically attractive and economically viable method of improving the surface layer of materials. Since the surface of the material controls the life of many applications, the goal is to develop a wide range of different functional properties of the basic substrate, including physical, chemical, electrical, electronic, magnetic or mechanical. As part of surface engineering, thermochemical processing uses thermal diffusion to incorporate non-metallic or metallic atoms on the surface of a material to modify its chemistry and microstructure (Fig 1).

The process is carried out in solid, liquid or gaseous media with one or more simultaneously active chemical elements. For the majority of thermochemical treatments, the mechanism comprises a decomposition of solid, liquid or gaseous species, the splitting of gaseous molecules to form nascent atoms, the absorption of atoms, their diffusion in a metallic network and reactions in the substrate structure to modify existing phases or form new phases. Since in the scale process industry, the whole piece is subjected to high temperatures, the superficial diffusion is superimposed on changes in the volume of the material which, for some treatments, may involve phase transformations, which adds to the complexity.

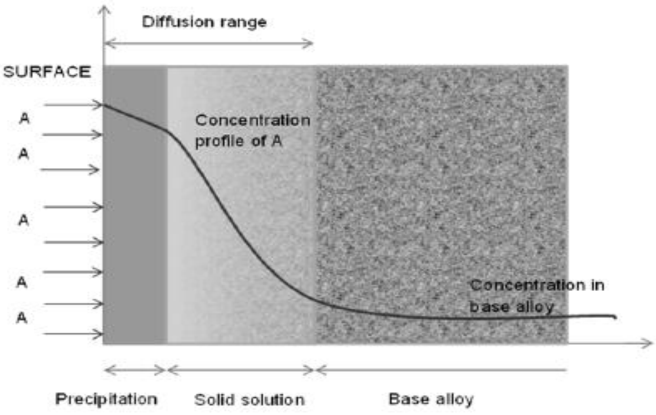


Fig. 1. Principles of thermochemical treatment showing a distribution of the chemical element A inside an alloy as well as typically modified sub-surfaces.

2. Nitriding

Nitriding has been and remains the main thermochemical treatment which, together with ferritic nitrocarburization, represents the dominant volume of industrial surface modification technologies. The treatment leads to a nitrogen incorporation at the surface of the steel when in the ferritic state. In commercial applications, the typical modified area is up to 200-300 μm thick and rarely exceeds 600 μm. Its impact on the surface hardness distribution, in terms of maximum value and depth of penetration, compared to other heat and thermochemical treatments. No additional heat treatment is required after nitriding and component surface hardness, wear resistance, improved corrosion resistance and fatigue resistance. [1]

3.Nitrocarburation (ferritic nitrocarburizing)

Nitrocarburizing, nitrogen and carbon are introduced to the ferritic steel surface at temperatures generally between 500 and 580°C. The general classification of thermochemical treatments involving nitrogen and / or carbon. In one terminology, the high temperature equivalent of ferritic nitrocarburization is called austenitic nitrocarburization. There is also a ferritic carburizing term, describing the carburizing process at temperatures of the ferritic state. [2]

3.1 Structure of the surface layer

During iron nitrocarburization, the microstructural evolution of the combination layer begins with the formation of carbon-rich cementite and develops in the direction of the carbon-rich and carbon-poor phases ε and γ '[3]. Both steps are a consequence of nitrogen solubility in α-Fe with respect to carbon and lower transfer of nitrogen from the gas into the solid phase. The combination layer is generally a combination of iron carbonitrides ε-Fe_3 (N, C) 1 + x and γ'-Fe_4 (N, C) $_{1\text{-}z}$ with cementite θ-Fe_3C (Table I) [4] [5]. As during the nitriding, under the combination layer, the diffusion zone is formed, the carbon and nitrogen being dissolved in the ferritic matrix. It is well documented that the best properties are obtained when the combination layer mainly contains the single phase ε (Figure 2a). The combination layer, typically in the 20 μm range, leads to significant improvements in hardness, wear resistance and corrosion. The presence of ammonia in a gaseous nitrocarburizing atmosphere affects the structure of the combination layer and the presence of Fe_3C cementite. During ferritic cementation of iron at a temperature of 550 ° C in gaseous atmospheres containing a certain amount of NH_3, massive layers of Fe3C cementite can be grown [6]. In order to generate thicker layers, the nitrocarburizing process is conducted at temperatures exceeding the Fe-N eutectoid point of 590 ° C. After austenitic plasma nitrocarburization at 700 ° C. for 3 h at 0.45%, the C-steel layer mainly contains the ε-Fe $_{2\ 3}$ (N, C) phase, but unlike the ferritic nitrocarburizing process, the austenite layer is form between the ε phase and the diffusion zone (Figure 2b) [7].

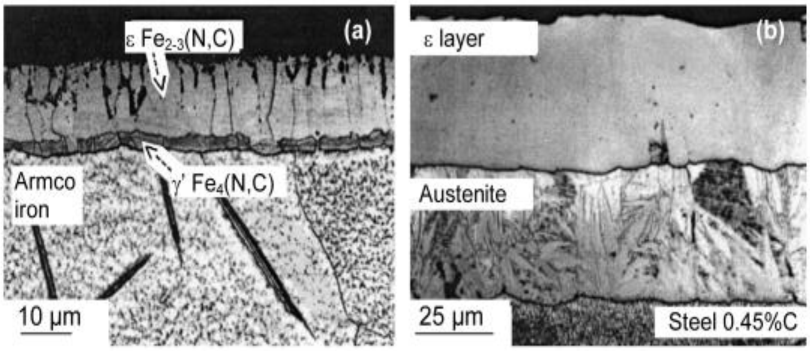


Fig. 2. Differences in microstructure after nitrocarburizing at low temperature and high temperature plasma in an atmosphere of 87% N2 + 8% H2 + 5% CO2: (a) Fer Armco at 570 ° C for 3h; austenitic plasma nitrocarburization at 700 ° C. for 3 h at 0.45% C [7].

The combination of nitrocarburizing and plasma oxidation has advantages in terms of resistance to surface corrosion [65]. Carbonitrided SKD61 steel with a combination layer of 10 μm thick (mainly ε-Fe2-3 (N, C) and low levels of γ'-Fe4 (N, C) diffusion layer) and a thickness of 200 μm subjected to plasma oxidation at 500 ° C for 1 h creates 1-2 μm thick layer of magnetite Fe3O4 above the combination layer [8]. According to the anodic polarization test, a significant improvement in the corrosion resistance of the steel is obtained.

Table 1. Characteristics of the phases in the Fe-N-C system at 580-590 ° C

Phase	N (at.%)	C (at.%)	Cristallography	Atom arrangement
α–Fe θ –Fe$_3$C γ – Fe$_4$N$_{1-z}$ ε – Fe$_3$(N, C)$_{1+x}$	0-37 0 25 19.4-20 <0.7 15-33	0-0.02 0 - 8	Fe bcc Complicated Fe orthorhombic Fe fcc	N, C in octahedral sites C in two-headed Trigonal prisms N ordered in the central octahedral sites

4. Experimental procedures

After degreasing and preheating to 350 ° C., the samples are treated at a temperature of 580 ° C. in a bath of molten salts for 10 h, cooled with oil and then stripped to remove the salts deposited on the surface.

Prior to nitrocarburizing treatment, the rectangular 4 mm thick specimens were cleaned with ethyl alcohol and dried. For metallurgical characterization (Chemical analysis and metallographic observation), mechanical characterization by Vickers microhardness.

Table 2. Spectral analysis of the chemical composition was performed on the six specimens to confirm the chromium content of the selected alloys.

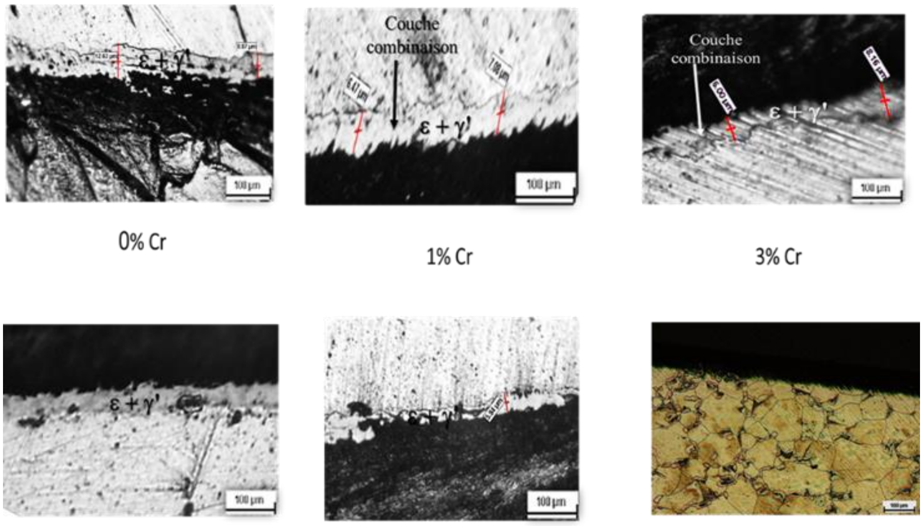
% metal	0% Cr	1% Cr	3% Cr	5% Cr	8% Cr	12% Cr
Si	0.01	0.000	0.000	0.000	0.020	0.060
Mn	0.380	0.09	0.100	0.100	0.250	0.250
P	0.004	0.004	0.006	0.004	0.009	0.004
S	0.045	0.004	0.004	0.005	0.016	0.018
Cr	**0.050**	**1.020**	**2.85**	**4.830**	**7.730**	**11.83**
Ni	0.040	0.02	0.10	0.110	0.020	0.030
Mo	0.010	0.000	0.000	0.000	0.000	0.003
Al	0.059	0.000	0.000	0.000	0.012	0.000
Cu	0.045	0.023	0.027	0.029	0.034	0.028
Co	0.000	0.004	0.007	0.000	0.005	0.007
Ti	0.004	0.000	0.000	0.000	0.0025	0.003
V	0.000	0.002	0.007	0.0007	0.006	0.013
N	-	-	-	-	-	-
Fe	**99.055**	**99.571**	**94.641**	**94.622**	**91.599**	**87.568**

4.1 Experimental results and discussion

The results of the different characterizations:

4.1.1 Metallographic Observation

The optical microscope examination was performed on cross-sections of the previously mechanically polished samples and the felt disc up to 1 μm and then etched with 4% nital.



0% Cr

1% Cr

3% Cr

8% Cr

5% Cr

12% Cr

Fig.3 .Optical micrograph of six iron-chromium alloys treated with salt bath for 10 h of 580 ° C.

The micrograph clearly shows the presence of two layers:

1). A two-phase combination layer at the surface consisting of carbonitrides $\varepsilon - Fe_{2\_3}$ (C, N) on the surface and γ'-Fe_4 (C, N) in the under layer.

2). A diffusion layer of nitrogen and carbon whose thickness depends on the chromium content of the studied alloy.

Table 3. Result of the measurements of the thickness of the combination and diffusion layers.

	Epaisseur des couches **µm**	
Matériaux	**DUFFUSION**	**COMBINAISON**
Fer pur	280	13
1% de Cr	250	11
3% de Cr	240	8
5% de Cr	200	6.5
8% de Cr	160	4
12% de Cr	140	1

The results of the measurements of the thickness of the layers show:

. The thickness of the diffusion layer is all the lower as the chromium content is high.

. It is noted that the total thickness of the combination layer on the surface is higher the lower the chromium content.

4.1.2 Vickers microhardness

A charge of 100grf was applied for 10 s (HV 0.1 / 10) at each measurement point, at an ambient temperature of 25 ° C, for the measurement a 30 µm pitch was used.
Microhardness values are shown on a table as follows:

Table 4. Vickers microhardness measurements as a function of depth

D (mm)	**Pure Iron**	**1% Cr**	**3 % Cr**	**5% Cr**	**8% Cr**	**12% Cr**
30	370	418	506	543	650	688
60	374	370	442	489	630	612

120	365	355	418	351	510	320
150	355	348	361	315	300	250
180	341	330	302	285	298	247
210	328	310	285	258	295	245
240	320	270	240	255	293	243
270	317	265	235	253	291	241
300	315	260	230	252	290	240
330	312	250	229	250	289	238

Table 4 shows the results of measurements of the Vickers microhardness profiles (under a load of 100 grams) made on the different nitrocarburized specimens.

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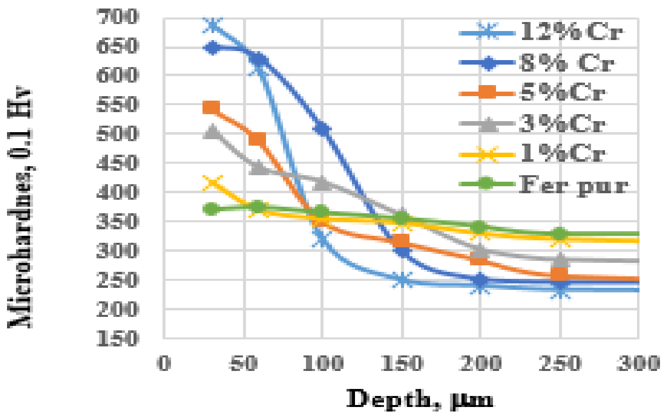

Fig. 4 Vickers nitrocarburizing microhardness profile versus different nitrocarburized alloys 10 hours at 580 ° C.

Figure 3 shows the overlap of the different profiles performed.
The profiles produced show the following observations:
1. The microhardness at 30 µm of the edge is even higher than the chromium content is high.
2. The diffusion depth is even lower as the chromium content is high.

4.2 .Discussion

4.2.1 .Metallographic Observation

We previously showed that after nitrocarbureas 10 hours at the temperature of 580 ° C, the combination layer is two-phase and the total thickness of the combination layer depends on the chromium content of the alloy studied.

The higher the chromium content, the lower the thickness of the combination layer is due to the migration of chromium atoms to the surface and their combination with the nitrogen resulting from the decomposition of CYANURS (KCN_ Na CN).

Surface formation of CrN and / or Cr2N nitrides blocks the kinetics of nitrogen diffusion. This is the reason why the depth of the diffusion layer is lower when the chromium content is high.

The absence of the combination layer in the case of the 12% Cr alloy is due to the formation of a thick layer of CrN nitrides and or Cr_2N the concentration of nitrogen at the surface becomes lower and carbonitrides ε and γ 'cannot be formed.

Table 5. Combination layer thickness comparison

Nuance	XC45	42CD4	Pure Iron (0%Cr)
Combination layer thickness in (µm)	17	12 ,76	13

4.2.2 .Microhardness Profiles

A study was carried out by Leroy [9] on nitrated Fe-Cr binary alloys at 580 ° C. by ionic route, which made it possible to define three modes of interaction of nitrogen with chromium from the microhardness profiles.

- Low Interaction: 0 - 3% Cr
- Mean Interaction: 3 - 5% Cr
- Strong Interaction: 5 - 12% Cr

Based on the work of this author we presented in Figure 5, 6, 7, the microhardness profiles according to the type of interaction.

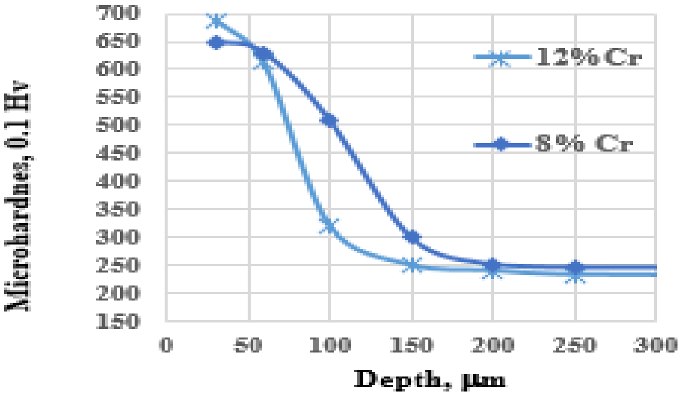

Fig.5 The profile of the strong interaction

The profiles in Figure 5 are related to alloy 8 and 12% Cr and a total depth of:

- 140μm to the 12% Cr alloy
- 160μm to 8% Cr alloy

These layer depths are about 100 μm lower compared to pure iron, which explains the strong interaction mode for these alloys.

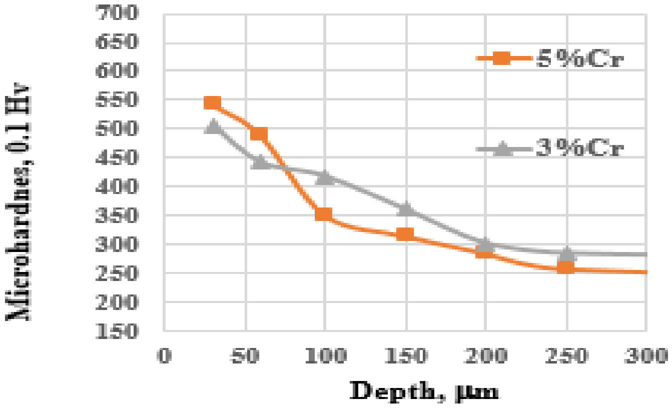

Fig.6 The profile of the mean interaction

The profiles of Figure 6 are related to alloy 5 and 3% Cr and a total depth of:

- 200μm to the 5% Cr alloy
- 240μm to 3% Cr alloy

the mode of interaction is medium and the difference observed in the case of the alloy at 5% is about 50 μm in pure iron which explains the strong mode of interaction for these alloys (5% Cr, 3% Cr).

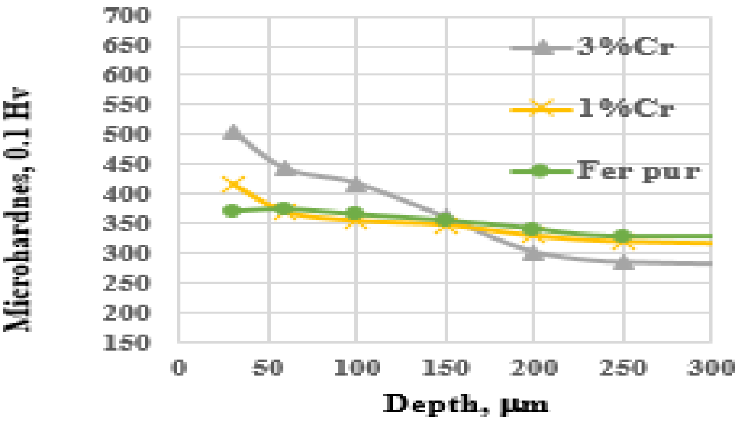

Fig.7 The profile of the low interaction

The profiles in Figure 7 are related to alloys 0 and 1 and 3% Cr and a total depth of:

- 140 µm to the alloy of 0% Cr
- 160 µm to 1% Cr alloy
- 240 µm to 3% Cr alloy

These layer depths are about 1 µm lower than pure iron, which explains the strong interaction mode for these alloys (0% Cr, 1% Cr, 3% Cr).

The interaction between chromium and nitrogen in the 3% Cr shade favors the process of germination of the precipitates (increase in the number of CrN nitrides compared to the grade containing 1% Cr), which explains the observed hardening more important , at the expense of the diffusion of nitrogen in the ferritic phase (less depth of nitriding).

5. Conclusions

The results obtained have allowed us to conclude that:

- The presence of alloying elements promotes the structural hardening of the material by precipitation of nitrogen in the form of nitrides and or carbonitrides.
- The configurations of layers formed and their thicknesses depend on the chromium content chosen.
- The higher the chromium content, the lower the concentration gradient of nitrogen in the diffusion layer, and the lower the thickness of the combination layer at the surface.
- The results of metallographic observations indicate a two-phase combination layer on the surface of the nitrocarburize material. The thickness of the total combination layer decreases as the chromium content increases.
- Depending on the concentration of the nitrogen, when combined with iron, it can form, at the extreme surface, a combination layer consisting of carbonitrides Fe4 (C, N) and / or Fe2-3 (C, N). This thin layer (<30 µm), can be single-phase or two-phase, has a high hardness; it is followed in depth by a diffusion layer.
- The presence of alloy elements that have a high affinity for nitrogen in steel causes a layer of nitrides and / or carbonitrides (CrN, Cr2N) that hinder the diffusion of nitrogen into the diffusion layer.
- The microhardness profiles for nitrocarburized alloys show three types of strong interaction (for alloys studied 8 and 12% Cr), a mean interaction (for alloys at 3 and 5% Cr and a weak interaction (for 1% Cr alloy).

6. References

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