Non-Toxic Environment for Ferritic Nitrocarburising Process

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Experimental research aimed to find a solution for replacing components with high toxicity (or generating such components as a result of reactions occurring in the environment at processing temperatures) from the environments used for ferritic nitrocarburising process (FNCP) with non-hazardous components, but extremely active during the process. In the temperature range in which this type of processing is applied (lower than the eutectoid transformation temperature in the Fe-N phase diagram), the most commonly used media are liquid or gaseous; liquid ones contain toxic components (sodium or potassium cyanates/ cyanides), and gaseous ones require complex equipments. Packing is extremely rarely used, but in this case pack-mix contain toxic components (15 ÷ 20 wt.% sodium or potassium ferrocyanide). Urea also called carbamide (CO $(NH_2)_2$) is the active component in the pack-mixing proposed to be used for FNCP. Carbamide is used in low temperature cyanidation thermochemical heat treatment (liquid FNC), together with sodium or potassium carbonates, resulting in very toxic reaction products (sodium or potassium cyanates). Compared to cyanidation, in the version proposed in the paper, the carbamide does not react with carbonates because they are not found in the composition of the environment but decomposes in the presence or absence of oxygen (by a disproportionation reaction) with the formation of some gas molecules interesting for the process. It has been concluded that the use of carbamide together with two other components, activated charcoal (having a triple role - dispersing, storage, surface saturation) and respectively ammonium chloride as surface reaction activator, is an effective solution for achieving the desired goals by applying this type of thermochemical processing to a wide range of products made of quality steels up to alloy miscellaneous steels.

Keywords: ferritic nitrocarburising (FNC), average toxicity, ionic adsorption mechanism

The increase of the exploitation performance of large categories of steel products (quality steels, cemented steels, special steels, tool steels, miscellaneous steels, cast iron (grey irons, ductile irons), et ceteras, is assured by FNC thermochemical heat treatment application, in the temperature range below the eutectoid transformation temperature according to the Fe-N phase diagram [1-6,15].

The nitrocarburizing temperature applied to alloyed and high alloyed steels must be less than or equal to that of the tempering, so that the core structure of the products is not affected; for the other mentioned steels the degree of damage to the core characteristics is low and insignificant in relation to the benefits conferred by the improvement of the layer by nitrocarburation, due to the relatively short time of isothermal processing [1].

In the case of cemented steels, the application of nitrocarburising, either after carburising or after carburising and quenching, is of particular interest [1,10,12].

The activ media used for nitrocarburising are extremely varied: the solids or liquids have a common denominator - the high content in toxic components, initially or generated during thermochemical process; the gaseous ones have as their main component ammonia, similar to nitriding, and propane / methane / endogas (Nitemper & Nikotemper procedure) / exogas exogas (Nitroc procedure), as a carbon source [4,12,14]. Since processing variants in gaseous media require high investment due to strictly specialized equipment, processing variants in liquid and less solid media are the most commonly used. Liquids and solids used to carry out nitrocarburisation use toxic-salt components containing the *CN* (NaCN, KCN, $Na_4Fe(CN)_6$, NaOCN, KOCN), so called Tenifer &Taftreiding procedures, - Tenifer and Taftreiding processes, or products resulting from the direct reaction between urea and Na_2CO_3 / K_2CO_3, mainly important as it drastically restricts these processing variants.

Experimental part

Thermochemical processing (i.e. FNCP) was performed on pure technical iron matrices (Fe-ARMCO) in the temperature range of 350÷560°C with 3÷24 h resting time, followed by furnace cooling up to 150°C and subsequently air cooling.

The samples were placed in steel boxes, packed in a powder mixture. The mixture of powders consisted of 50% carbamide, 48% activated charcoal and 2% NH_4Cl, was milled in the tronconic milling for 30 min at 150 rpm [8].

The heat treatment furnace is equipped with an automatic temperature monitoring system.

The results were investigated by optical microscopy (OM) system, consist of a REICHERT UnivaR microscope and a materiallographic software - OmniMet Enterprise, from BUEHLER) and by scanning electron microscopy (SEM) on a FEI Quanta Inspect F50 microscope.

Results and discussions

Carbamide is commonly used in FNCP as a source of nitrogen and carbon respectively, in a number of technological variants, such as: in the Na_2CO_3 / K_2CO_3 salt baths [1-5,9], or impregnated from an aqueous solution in a small spongy mica medium (U.S. Patent 4,119,444). Regardless of the processing variant, the carbamide is not toxic at the begining of the process but generates highly toxic components due to the reactions in the salt baths used for the low temperature cyanidation (≤ 590 °C). Also results cianates, which in turn generates sodium or potassium cyanides, and when the carbamide in an

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aqueous solution impregnates a small spongy mica, forms fulminic acid (HCNO) with very high toxicity as well.

The analysis of the possible mechanisms by which the carbamide can be a direct source of nitrogen and carbon in the absence of carbonates or other toxic compounds generates the following aspects:

-At FNCP temperature the carbamide may undergo a disproportionation reaction (1) or decompose in the presence of oxygen (2), thereby generating ammonia, carbon monoxide or carbon dioxide, nitrogen and hydrogen (1) or decomposing in the presence of charging oxygen (2), thereby generating ammonia, carbon monoxide or dioxide, nitrogen and hydrogen.

$$2CO(NH_2)_2 \rightarrow 2\mathbf{CO} + 2\mathbf{NH_3} + N_2 + H_2 \quad (1)$$

$$2CO(NH_2)_2 + O_2 \rightarrow 2CO_2 + 2\mathbf{NH_3} + N_2 + H_2 \quad (2)$$

Reactions (1,2) take place at temperatures above the melting point of the carbamide (133 °C), which claims the use of a melt dispersion / storage component.

The active charcoal can play such a role (reactions 3 and 4), while contributing to maintaining the uniformity of the carbamide initially distribution in the volume of the solid mixture powder with direct effect on the generation of active nitrogen and carbon, necessary for superficial saturation.

$$C + CO_2 = 2\mathbf{CO} \quad (\Delta G^{550^\circ C} = -26{,}43\, KJ/mol) \quad (3)$$

$$C + 2H_2 = \mathbf{CH_4} \quad (\Delta G^{550^\circ C} = 0{,}272\, KJ/mol) \quad (4)$$

The two reactions are highly thermodynamically probable at temperatures below 550 °C because the free reaction enthalpy is always negative.

- The nitrogen generating sources necessary for the saturation in the FNCP are the ammonia resulting from the decomposition of the carbamide but also from the decomposition of the ammonium chloride (6) used as an active component (source of ammonia) but also by the surface cleaner/activator (HCl). Active carbon sources (9,10) are carbon monoxide resulting from the decomposition of the carbamide or as a result of the reactions caused by the presence of charcoal (3,4,7,8).

$$2NH_3 = N_2 + 3H_2 \quad (\Delta G^{550^\circ C} = -82{,}2\, KJ/mol) \quad (5)$$

$$NH_4Cl = \mathbf{NH_3} + HCl \quad (\Delta G^{550^\circ C} = -46{,}1\, KJ/mol) \quad (6)$$

$$C + O_2 = CO_2 \quad (\Delta G^{550^\circ C} = -395{,}6\, KJ/mol) \quad (7)$$

$$CO_2 + H_2 = \mathbf{CO} + H_2O \quad (\Delta G^{550^\circ C} = 8{,}668\, KJ/mol) \quad (8)$$

$$2CO = \mathbf{C'} + CO_2 \quad (\Delta G^{550^\circ C} = -26{,}43\, KJ/mol) \quad (9)$$

$$CH_4 \mathbf{=} \mathbf{C'} \mathbf{+} 2H_2 \quad (\Delta G^{550^\circ C} = -0{,}272\, KJ/mol) \quad (10)$$

Were ***C'*** represents the active carbon atoms capable of the metallic surface saturation, subjected to processing.

In relation to the actual nitrogen source, the opinions are divided, the overwhelming majority of the theories, starting from the high thermodynamic stability of the nitrogen molecule (N_2 '$\rightarrow$ N + N; $\Delta G^{550} = +487KJ/mol;\ \Delta H^{550} = +951.4KJ/mol$), denies the possibility that under these conditions the atomic mechanism of adsorption acts, the mechanism accepted as predominance being the ionic one (theory of electrostatic forces) [6,7].

The NH_3 decomposition (11) is a highly endothermic one, the amount of energy necessary for its unfolding is of 11.2 eV, in contrast to the ionization reaction of the ammonia molecule (12) which unfolds with energy release (+ 2.85eV).

$$NH_3 \longrightarrow N + 3/2H_2 \quad (11)$$

$$NH_3 + e^- \longrightarrow NH_{3-} \quad (12)$$

As a result, in pack FNCP, similar to the gaseous one, the ionic adsorption mechanism [7,16] acts, the only source of nitrogen supply being ammonia through its anions type (NH_3^-) [6,7,16,17]. This type of ionization (12) is highly probable in the case of iron matrices presenting submicron oxide films, in which case the energy required to pull the electrons of the double electric layer is of 3.0eV, below the energy level reached by the electrons in this zone in contact with the ammonia gas molecules at the thermochemical processing temperature (560 °C), ~ 3.0295eV [6,16,17,18].

In the present work ammonium chloride has the role of cleaning/activating the surface subjected to thermo-chemical processing by the possible oxides. At the same time, in the presence of hydrochloric acid vapors resulting from the thermocatalytic dissociation of the ammonium chloride molecules (6), it becomes highly probable the formation of the iron dichloride on the metal surface to be processed (13) with the release of a enough amount of heat to stimulate the electronic emission and thus touch up reaction (12), i.e. the initiation of the nitrogen saturation process.

$$Fe + 2HCl = FeCl_2 + H_2$$

$$(\Delta G^{550^\circ C} = -38{,}287 KJ/mol; \Delta H^{550^\circ C} = -145{,}8 KJ/mol) \quad (13)$$

It is noted that the reaction (13) can be carried out particularly energetic even at much lower temperatures, the thermal effect remains at a particularly high level

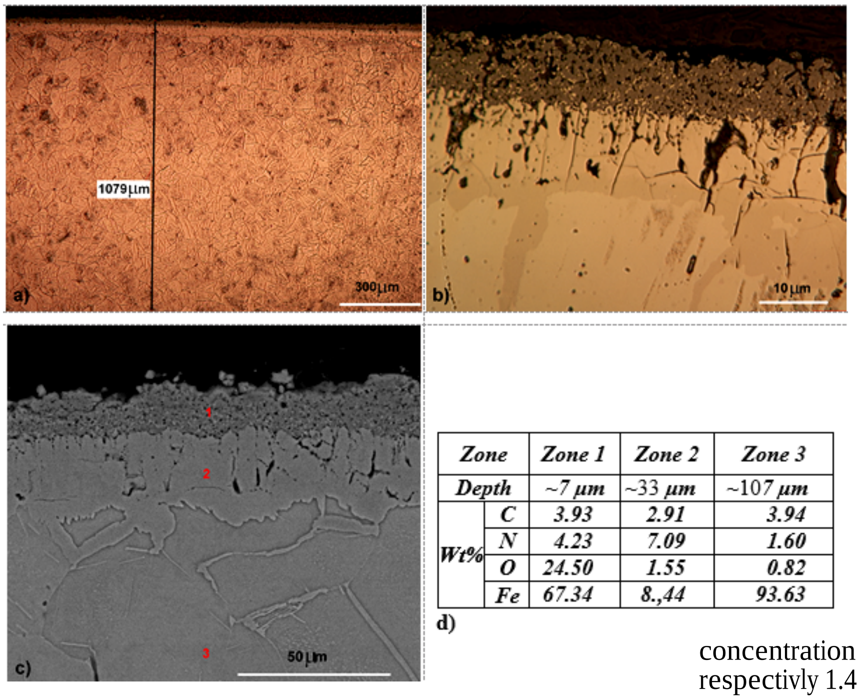
(ΔG^{550} = -64.855KJ/mol; ΔH^{550} = -149.3KJ/mol).

This latter finding is experimentally confirmed by the results obtained in the pack FNCP at 350 °C (fig. 2). In the absence of ammonium chloride the theoretical nitrogen saturation would not have been possible, because the energy restored the electrons in the double electric layer of the oxidized iron matrix would have been below the minimum required to exceed the potential barrier (~ 2.98eV compared to a minimum of 3.0eV required for the jump) [6,17]. In the presence of NH_4Cl, because of the large amount of energy released as as the efect of $FeCl_2$ synthesis (~ 149KJ/mol, i.e. ~ 9.3.1023eV/mol), the adsorption process is initiated, the dimensions of the layer obtained being relatively small (10÷12µm in 3 h) due to the low value of the the diffusion coefficient of nitrogen in the ferrite at this temperature.

Experimental research on Fe-ARMCO has confirmed that $CO(NH_2)_2$ can be used as a source of nitrogen and active carbon in order to saturate the surface metal products in the relatively low temperature range (below the eutectoid transformation from the Fe-N phase diagram) [8].

The OM and SEM analyses (fig. 1) on the layers obtained by pack FNCP reveals the presence of some structures with typical phase compositions of such a process [11,13,15].

The microstructure analyses of the layer obtained under these processing conditions (560°C/24h) reveals an extremely well developed diffusion area (a total layer of ~ 1079µm, determined by ~ 45 µm/h, the growth rate of the layer), with γ-type nitride separations, as it shown in fig. 1a).



Zone		Zone 1	Zone 2	Zone 3
Depth		~7 μm	~33 μm	~107 μm
Wt%	C	3.93	2.91	3.94
	N	4.23	7.09	1.60
	O	24.50	1.55	0.82
	Fe	67.34	8.,44	93.63

Fig. 1 Cross section microscopy of Fe-ARMCO FNCP (560 °C / 24h); a) the total layer thickness; b) morphology of the layer; c) SEM image of the layer; d) chemical elemental composition (EDS) in the micro-zones represented in c)

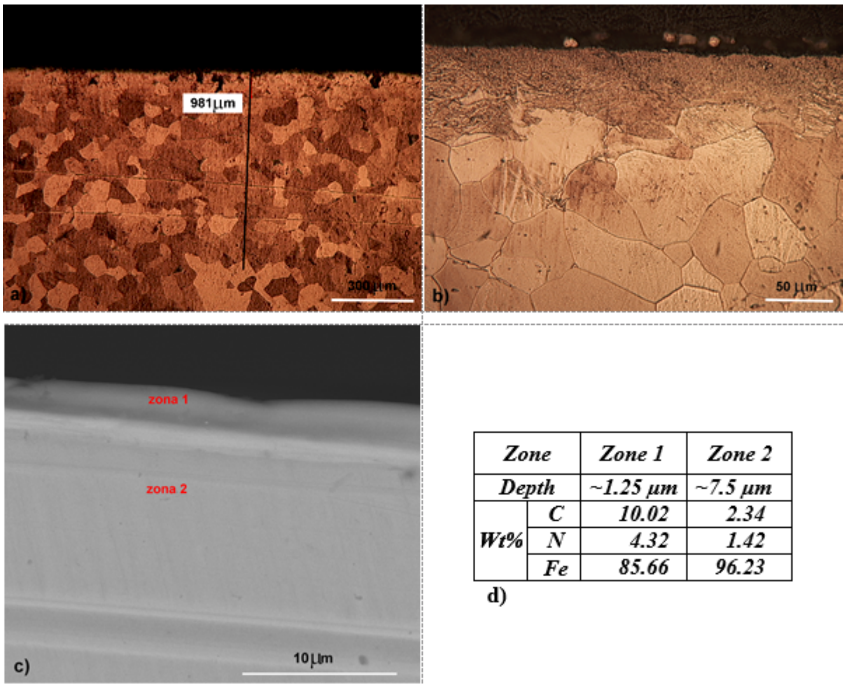
The cause of the porosity appearance in the superficial layer areas, as it shon in fig. 1b), is dictated by the high nitrogen concentration, which can be corrected by adjusting the activity of the environment (proportion of carbamide from the powdered solid mixture) and processing parameters. As it shown in fig. 1.c), d), the mass percentage of nitrogen increase from 4.23 wt% (zone 1) to 7.09 wt% (zone 2), for then to decrease to1.60 wt% (zone 3). In this case, the substrates having about two times the thicknesses on the same metal matrix as compared to those obtained in the gaseous atmosphere.

It has been found that a decrease of the FNC temperature up to 350 °C, which is anyway above the carmabide meling point, preserves its nitriding potential at a high level (fig. 2a). The experimental results on the similar samples, in the same conditions process (Fe-ARMCO, pack mixture: 50% carbamide, 48% activated charcoal and 2% NH$_4$Cl), but at a maintenance time of only 3 h, confirms a nitrogen concentration of 4.32 wt% at 1.25 μm (zone 1) and and respectivly 1.42 wt% at 7.5 μm (Zone 2), as it shown in fig. 2 b, c).

Experimental researches confirmed that the medium remains active and its use for high temperature carbonitration (austenitic nitration). In this case the thermochemical heat treatment temperature was 900 °C, with 8 h maintenance time.

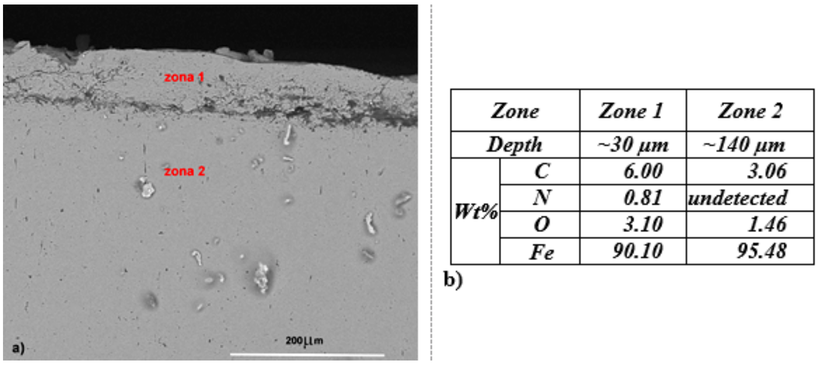
Under these process parameterss, the carbon concentration determined by EDS at a depth of ~ 30 μm is*-*** 6.00 wt% and nitrogen of ~ 0.81wt%, because at a depth of ~ 140μm the carbon percentage decrease to 3.06 wt % and nitrogen is no longer detected (fig. 3).

When using a powder mix containing 50% carbamide, 48% activated charcoal and 2% NH$_4$Cl, at a temperature of 900 °C / 8 h, the layer obtained has ~ 200μm (25μm/h). Under these temperature conditions, the carbon concentration determined by quantitative chemical microanalysis at a depth of ~ 30μm of surface is ~ 6 wt% and nitrogen of ~ 0.81 wt%, so that ~ 140 μm of surface area carbon concentration decrease to ~ 3.06 wt% and nitrogen is no longer detected.



Zone		Zone 1	Zone 2
Depth		~1.25 μm	~7.5 μm
Wt%	C	10.02	2.34
	N	4.32	1.42
	Fe	85.66	96.23

Fig. 2 Cross section microscopy of Fe-ARMCO FNCP (350 °C / 3h); a) the total layer thickness; b) morphology of the layer; c) SEM image of the layer; d) chemical elemental composition (EDS) in the micro-zones represented in c)



Zone		Zone 1	Zone 2
Depth		~30 µm	~140 µm
Wt%	C	6.00	3.06
	N	0.81	undetected
	O	3.10	1.46
	Fe	90.10	95.48

Fig. 3 Cross section microscopy of Fe-ARMCO FNCP (900 °C / 24h); a) SEM image of the layer; d) chemical elementalntal composition (EDS) in the micro-zones represented in a)

Conclusions

Experimental researches has confirmed that carbamide in combination with activ carchoal and ammonium chloride, can generate a nontoxic medium that is particularly effective for surface nitrogen and carbon saturation in the lowered temperatures, that is below 590 °C. This process being assimilated to a ferritic nitro-carburisation (FNC).

Ammonium chloride added to the powder mixture composition used for FNCP plays an active role in stimulating adsorption processes by the large amount of energy supplied to the surface during the synthesis of the iron dichloride.

The pulverulent powder mixture used for FCNP can also be used for carbonitration (austenitic nitration).

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Manuscript received: 6.02.2018