International Journal of Computational and Experimental Science and ENgineering (IJCESEN)

Vol. 11-No.4 (2025) pp. 4707-4713
http://www.ijcesen.com

ISSN: 2149-9144

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Research Article

Thermodynamic modelling to predict phases in nitrided Steels Containing 0.2%wt. Aluminium and 1%wt. Chromium

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Article Info:

DOI: 10.22399/ijcesen.5334
Received : 05 October 2025
Revised : 15 December 2025
Accepted : 20 December 2025

Keywords

Nitriding heat-treated steels
ThermoCal
simulation

Abstract:

The hardening of nitrided steels can occur by the formation of Guinier-Preston zones or by precipitation of Nitrides or Carbonitrides which depends on the affinity of Nitrogen for chromium and the elements present in this alloy but also, to a large extent , the lattice constant of the formed precipitate.The present work is based on simulation and thermodynamic Calculation allowing to predict the phases likely to form, under the fixed conditions of pre-treatment (tempering at 863.15° K) and Nitriding Treatment (823.15 ° K). It is necessary to compare the calculated diagrams with the experimental results in order to understand the hardening mechanisms after nitriding and other properties of this alloy. The discussions focus on the thermodynamic aspects and kinetic effects of the phases formed in this alloy.

1. Introduction

When carbon is present in the form of carbides in steel, differences in growth kinetics of the formed layers can be observed related to the state of heat treatment undergone before nitriding.The treatment of steels in the annealed condition generally requires a longer nitriding time than that of a quenched and tempered state leading to a fine and dispersed distribution of the carbides. Obviously, the nature of the alloying element with which the carbon is combined will influence the process.In Fe-X binaries, nitrides are in FexNy form, whereas in the case of Fe-X-N alloys, the interaction between the alloying element X and nitrogen defines the precipitation mode. According to Leroy [1], to describe the action of the alloying elements on the hardness profile we often use the classification proposed by D.H Jack and B.J Lightfoot [2], which consists in grouping the elements into three main classes according to the type of interaction of the metallic element with nitrogen Figure 1.

Figure 2 shows the evolution of the nitrogen-alloying element activity coefficients f_N^X as a function of the content of alloy elements and confirms this work. These values represent the effect of element X on the solubility of nitrogen in ferrite. Indeed, elements with a negative activity coefficient gradient (Ti, V, Mo, Cr ...) tend to increase the solubility of nitrogen in ferriteAccording to Guerrero [3], [4] this effect is explained by the formation of the Guinier-Preston zone in ferrite, which are interstitial and substitutional clusters of atoms in the ferritic matrix. These zones constitute a first stage of precipitation, they tend to evolve and lose their consistency with the matrix to form equilibrium precipitates.According to the work of H.Michel [5] hexagonal nitrides mainly precipitate on the defects of the ferrite network and participate little in the hardening of the diffusion layer. Whereas those with a face-centered cubic structure with a crystal

parameter of around 0.404 nm precipitate in semi-coherent form can lead to significant hardening. Chromium nitride, close to these requirements, is particularly effective; Aluminum is a powerful stabilizer of ferrite [6] only leads to low hardness. Table1.The nitriding of steel reveals the existence of a variety of carbides, nitrides and carbo-nitrides of iron or alloying elements. Thus, despite the nitrogen-carbon interaction in iron, the nitrogen and carbon profiles drawn by Guerrero [4] for XC18 steel nitrided at 823.15 ° K, shows that the diffusion of nitrogen is accompanied by carbon backscatter (carbon is chased to the center zone)
Indeed, the diffusing nitrogen modifies the chemical potential of carbon, forcing it to migrate towards the center zone; it will also replace it in certain carbides: M.Confente and his Collaborators [10] point out that this mechanism could lead to pre-precipitation from alloying elements initially combined with M_3C carbide and which remained free once the carbon has migrated.

1 Thermodynamic Calculations

Phase diagrams were computed using the Thermocalc® program for a system in which the equilibrium between ferrite, chromium nitrides and N_2 gas at the metal surface was considered. The thermodynamic description of the gaseous phase contained in the SGTE Substances 1994 Database - SUB94 – was appended to the system's description contained in the SGTE Solid Solutions – SSOL – Database The calculation of the phase distribution at a tempering temperature of 863.15 °K of this grade of steel makes it possible to predict the existence of two types of carbides M_7C_3 and Cementite in the matrix: ferrite (BCC). Table2.By maintaining the chromium at 1% and varying the carbon content, we obtain the diagram of Figure 3, which presents two carbides M_7C_3 , M_3C_2 and Cementite, which would be stable at low temperatures
(< 750.15 ° K), beyond this temperature M_7C_3 and Cementite would be predominant.The diagram in Figure 4 treats the Fe-Cr system at 0.4 wt.% carbon and 0.2 wt.% Al. By varying the chromium we observe the presence of cementite and M_3C_2 in the ferrite matrix (BCC_A2) at low temperatures (< 750.15 ° K) at low chromium concentrations, M_7C_3 and M_3C_2 for higher chromium concentrations (> 2.5 wt.% Cr).The thermodynamic calculations and these diagrams make it possible to predict that the phases which may be present at the temperature 823.15 °K. In these steels are the two phases Cementite and M_7C_3 for carbon percentages of 0.4%wt, 0.2%wt of aluminum and 1% wt.Cr, beyond about 2% wt of chromium the only phase present in the ferrite matrix (BCC_A2) would be M_7C_3, Figure 3 and Figure 4.At constant temperature, the nitrogen supply modifies this configuration since CrN appears at the expense of the M_7C_3 phase, which disappears with the increasing nitrogen rate, Figure 5 and Figure 6The increase in the carbon content favors the presence of these cementite carbides and M_7C_3 , Figure 6 and Figure 10.We plotted the diagram of phase percentage as a function of the concentration of an element for a given composition, and for the following, we varied the nitrogen at the nitriding temperature of 823.15 ° K. Figure 7 shows the isopleth of the system Fe-1 wt. % Cr -0.4wt. % C -0.2 wt. % Al –N.Each curve shows the phase where it is stable and its equilibrium phase at any given nitrogen concentration. The diagram shows the amount of Chromium in each phase.The variation in the percentage of nitrogen indicates the evolution of the quantity of chromium present in the phases more particularly in the nitride CrN (FCC _A1 # 2) and the nitrides Cr_2N (HCP_A3 # 2).The variation in the percentage of nitrogen indicates that the carbide M_7C_3 disappears to the detriment of the nitrides CrN (FCC _A1 # 2) and Cr_2N (HCP_A3 # 2), with the increase of percentage of chromium Figure 7 and Figure 8.We plotted the diagram of phase percentage as a function of the concentration of an element for a given composition, and for the following, we varied the nitrogen, chromium then carbon at the nitriding temperature of 823.15 °K.Each curve shows the phase where it is stable and its equilibrium phase at any given Nitrogen

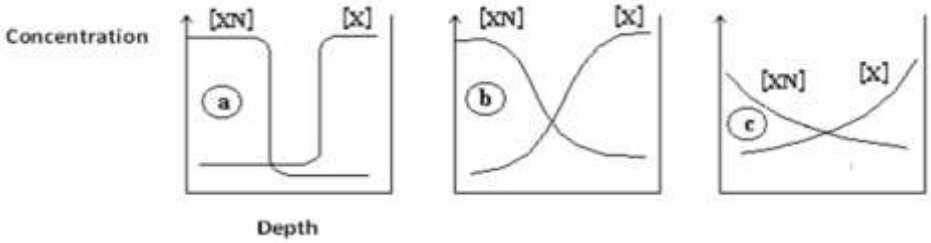

Figure 1. *Mode of interaction between alloying elements and nitrogen [3].*
a) Strong interaction (case of Fe-Cr with Cr> 5%, Fe-V with V> 1, Fe-Ti with Ti> 2%),
b) Average interaction,
c) Weak interaction (case of Fe-Cr to Cr = 1 to 2%, Fe-Mo with Mo <5%

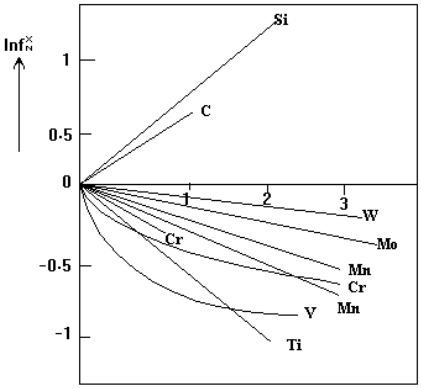

Figure 2. *The effects of alloying elements on the activity coefficient of nitrogen in iron at 773.15° K [3].*

Table1. *Crystallographic data of some nitrides [5],[7],[8],[9]*

Phases	**Bravais lattice**	**Lattice constant (nm)**	**Misfit parameters calculated according to the plane**	
			(010) Feα	**(001) Feα**
Fe_2N	Orthorhombic	a = 0.5530 b = 0.4835 c = 0.4425		
Fe_4N	Cubic Face Centered	a = 0.3790	0.065	0.32
Mo_2N	Cubic Face Centered	a =0.4169	0.028	0.45
Mn_5N_2	Hexagonal	a = 0.2834 c = 0.4451		
CrN	Cubic Face Centered	a = 0.4149	0.024	0.45
Cr_2N	Hexagonal	a = 0.4818 c = 0.4490		
Mn_4N	Cubic Face Centered	a = 0.3857	0.048	0.34
Si_3N_4	Orthorhombic	a =1.3380 b = 0.8600 c = 0.7740		
VN	Cubic Face Centered	a = 0.4139	0.021	0.44
AlN	Hexagonal	a = 0.3110 c = 0.4975		
TiN	Cubic Face Centered	a = 0.4244	0.047	0.48

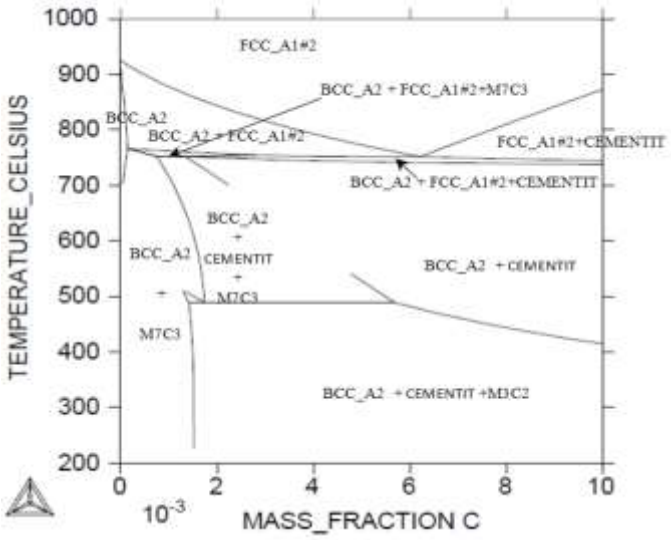

Figure 3. *Phase diagram of (Fe-1wt% Cr-0.2wt%Al) – C System;Thermo-Calc Calculations*

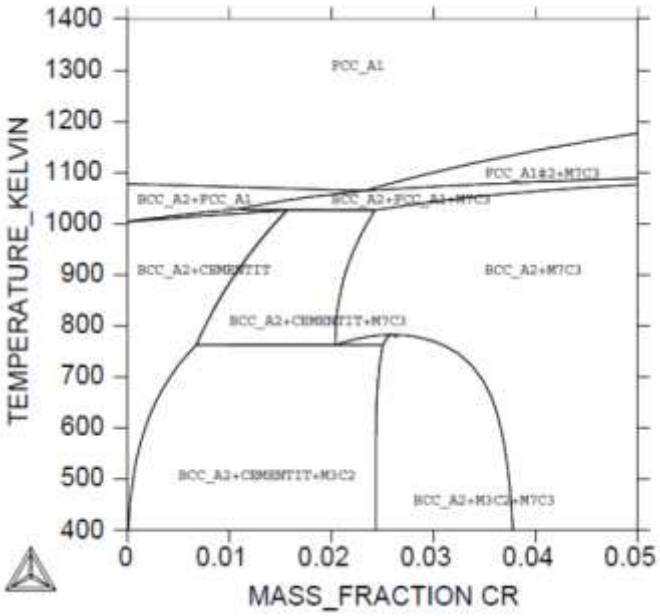

Figure 4. *Phase diagram of (Fe-0.4wt.%C-0.2wt.%Al) – Cr System; Thermo-Calc Calculations*

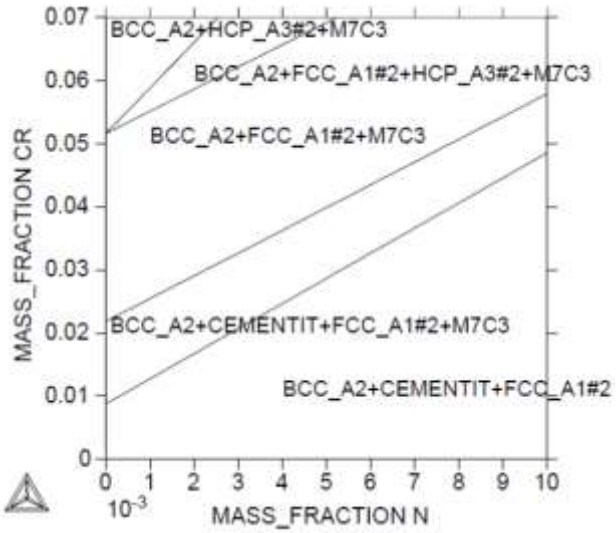

Figure 5. *Isotherm diagram of (Fe- 0.4wt.%C -0.2wt.%Al)-Cr –N system. At 823.15 °K; Thermo-Calc Calculations*

Table 2. *Distribution of phases in Steel: Fe-0.4wt. % C-0.2wt.% Al - 1 wt.% Cr*

	Percentage Phases i	**Bcc (%)**	**M_7C_3 (%)**	**CEMENTIT (%)**
	Molar %	93.24	0.24	6.52
	Weight %	94.54	0.18	5.28
Weight % Element In Phase i W(i, X_i)	**Fe**	99.59	47.09	79.75
	Cr	0.21	44.2	13.5
	C	0.003	8.72	6.76
	Al	0.2	0.00	0.00

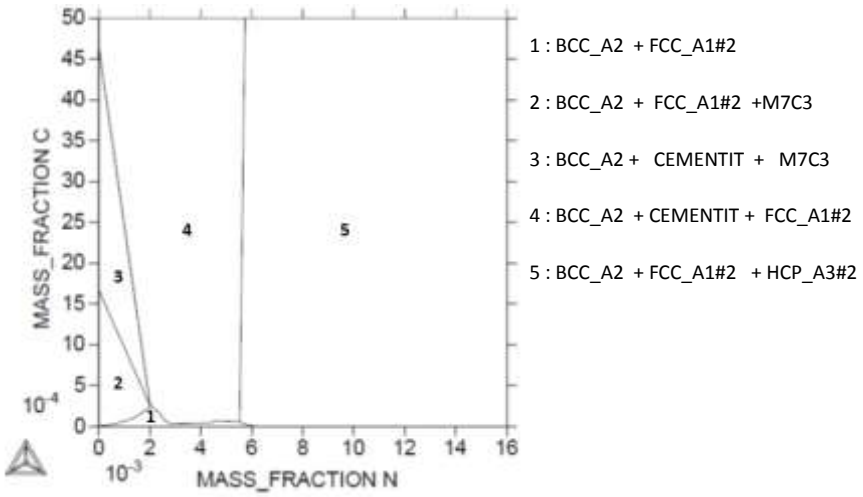

Figure 6. *Isotherm diagram of (Fe- 1 wt. % Cr -0.2wt. %Al.)- C –N. At 823.15 °K; Thermo-Calc Calculations.*

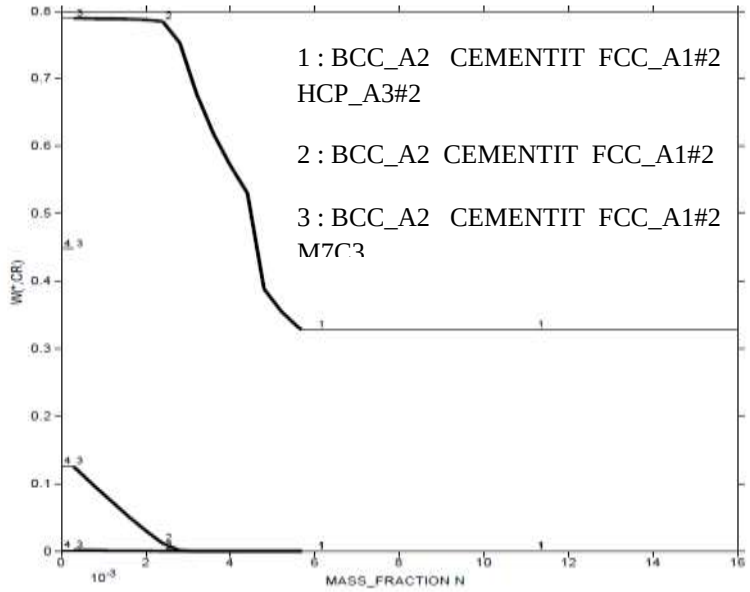

Figure 7. *Percentage chromium in the phases as a function of Nitrogen at 823.15 ° K, Fe-1 wt. % Cr -0.4wt.%C -0.2wt.%Al ; Thermo-Calc Calculations.*

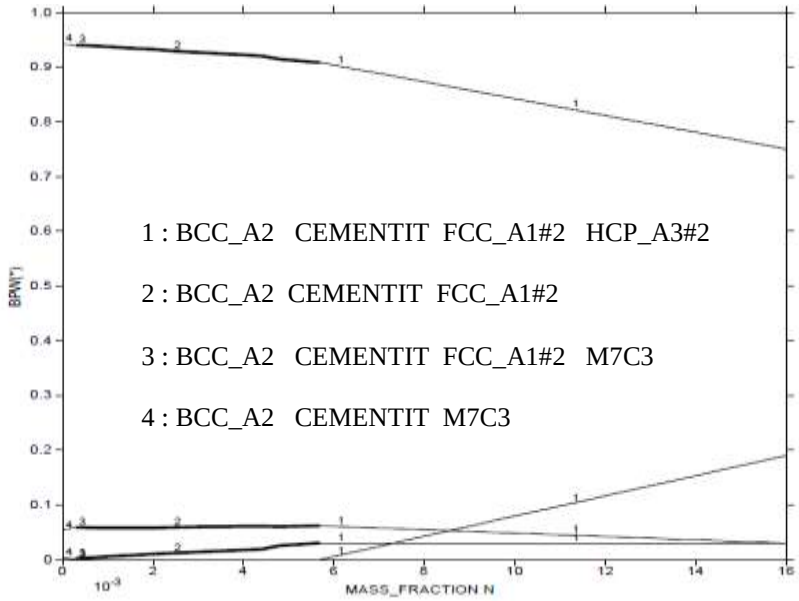

Figure 8. *Percentage of phases as a function of nitrogen at 823.15 ° K ,Fe-1 wt. % Cr -0.4wt.%C -0.2wt.%Al; Thermo-Calc Calculations.*

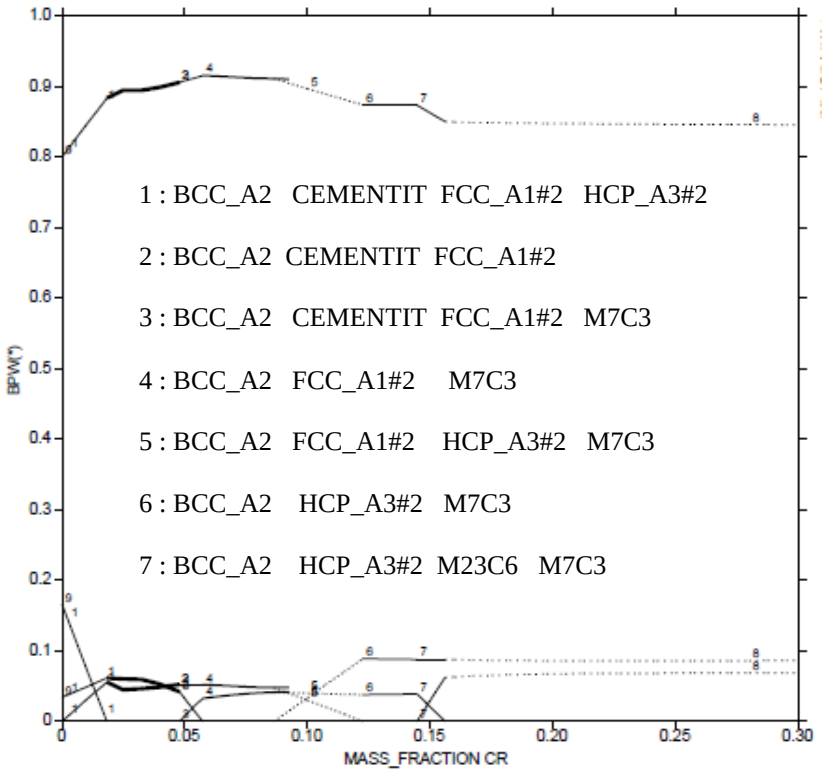

Figure 9. *Percentage of phases as a function of chromium at 823.15 ° C,Fe- 1 wt. % N - 0.4 wt. % C - 0.2 wt. % Al; Thermo-Calc Calculations.*

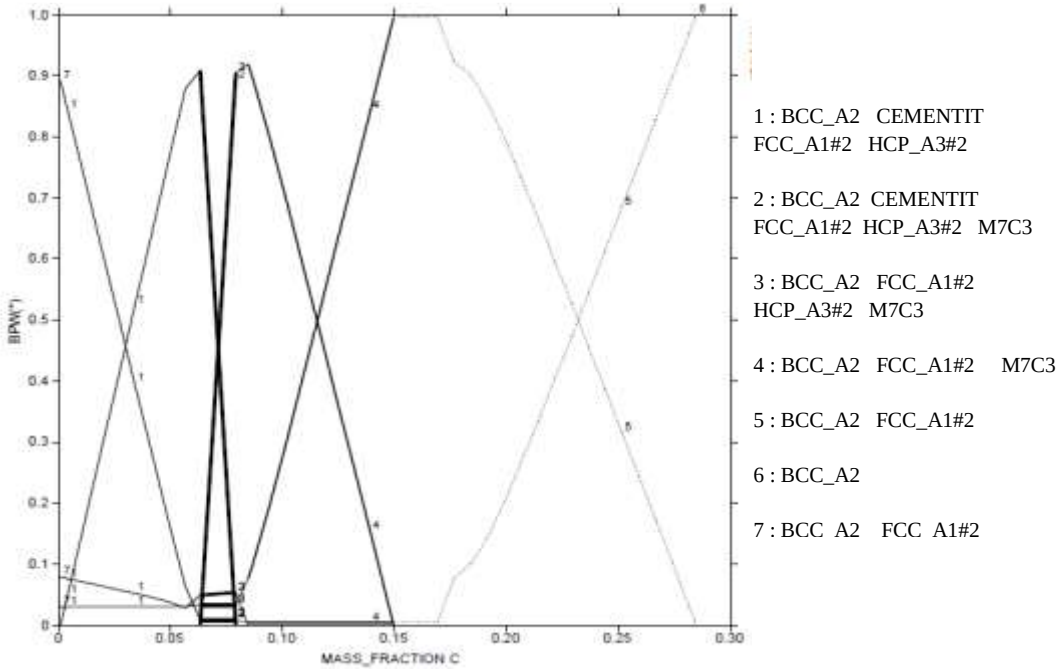

Figure 10. *Percentage of phases as a function of carbon at 823.15 °K, Fe - 1 wt. % N – 1 wt.% Cr - 0.2 wt.% Al; Thermo-Calc Calculations.*

concentration Figure 8, chromium concentration Figure 9 and carbon concentration Figure 10.At a fixed nitrogen level, the variation in the percentage of chromium indicates the presence of nitride CrN (FCC _A1 # 2) for chromium contents of up to 15 Wt.%, Stabilizes the carbide M_7C_3 and the domain of carbides $M_{23}C_6$ is pushed beyond 15 wt. % of chromium which could be (Cr, Fe) $_{23}C_6$ Figure 9.The variation in the percentage of chromium indicates the presence of cementite, which disappears beyond 8 wt. %

3. Conclusions

Thermodynamic calculations using Thermo-Calc made it possible to predict:

- The phases likely to exist in this alloy.
- For very precise thermodynamic conditions at the nitriding treatment temperature for this steel, the possible phases with the quantity of chromium present in these phases.
- For an evolution of the nitrogen, chromium or carbon levels the possible phases under the fixed conditions

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper
- **Acknowledgement:** T The author is grateful the Process Engineering Laboratory - Amar Tellidji University of Laghouat- Algeria for its help in using Thermo-calc, and Ministry of Higher Education and Scientific Research of Algeria.
- **Author contributions:** The authors declare that they have equal right on this paper.
- **Funding information:** The authors declare that there is no funding to be acknowledged.
- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.
- **Use of AI Tools:** The author(s) declare that no generative AI or AI-assisted technologies were used in the writing process of this manuscript.

References

[1] C.Leroy, "Etude des transformations de phases associées à la nitruration ionique des aciers alliés au chrome," *thesis , Nancy I, France*, 1983.

[2] B.J. Lightfoot, D.H. Jack, "Kinetics of nitriding with and without white layers Formation," *Heat Treatment. 73, the Met. Soc, pp.59-65, 1975.*

[3] M. Confente, "Etude physico-chimique et structurale de la nitruration par bombardement ionique à haute intensité d'aciers au carbone et acers alliés," *Thesis, Nancy I, France*, 1976.

[4] M.A.Cisneros Guerrero, "Etude des mécanismes d'interaction entre le manganèse, l'aluminium et l'azote dans les alliages ferreux : définition et mise au point d'une nouvelle classe d'aciers particulièrement aptes au durcissement superficiel par nitruration," *Thesis, INP- Nancy, France*, 1984

[5] H.Michel, "Nitruration de surfaces métalliques," *Journées d'Études Oléron 87, Les Éditions de Physique*, pp.465-486, june 1988.

[6] M.Hansen, K.Anderko, "Constitution of binary alloys," *2nd Edition. New-York: McGraw Hill*, 1958, isbn: 978-0070260504

[7] D.Ghiglione, C. Leroux, C.Tournier, "Pratique des traitements Thermochimiques," *Techniques de l'ingénieur, Traité De Matériaux Métalliques*, M1227, 1996

[8] M.A.J.Somers, R.M.Lankreijer, E.J.Mittemeijer, "Excess nitrogen in the ferrite matrix of nitrided binary iron-based alloys," *Philosophical Magazine. A*, vol.59, no 2, pp.353-378, 1989, doi: 10.1080/01418618908205064.

[9] M.Sennour, "Apport de la microscopie électronique en transmission et de la Spectroscopie EELS à la caractérisation de nitrures (AlN, CrN) dans le fer et l'alliage Fe-Cr," *Thesis INSA- Lyon, France*, 2002.

[10] M.Confente, H.Michel, Y.Pourprix, "Mise au point d'aciers économiques aptes à la nitruration," *Revue Traitement Thermique.197*, pp. 67-72, 1985.