

Predicting Microstructure Development During High Temperature Nitriding of Martensitic Stainless Steels Using Thermodynamic Modeling

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Thermodynamic calculations of the Fe-Cr-N System in the region of the Gas Phase Equilibria have been compared with experimental results of maximum nitrogen absorption during nitriding of two Martensitic Stainless Steels (a 6 mm thick sheet of AISI 410S steel and green powder compacts of AISI 434L steel) under N_2 atmospheres. The calculations have been performed combining the Fe-Cr-N System description contained in the SGTE Solid Solution Database and the gas phase for the N System contained in the SGTE Substances Database. Results show a rather good agreement for total nitrogen absorption in the steel and nitrogen solubility in austenite in the range of temperatures between 1273 K and 1473 K and in the range of pressures between 0.1 and 0.36 MPa. Calculations show that an appropriate choice of heat treatment parameters can lead to optimal nitrogen absorption in the alloy. It was observed in the calculations that an increased pressure stabilizes CrN at expenses of Cr_2N - type nitrides.

Keywords: *nitrogen absorption, high temperature nitriding, martensitic stainless steels*

1. Introduction

Nitrogen improves mechanical properties, wear and corrosion resistance of martensitic stainless steels¹. High nitrogen martensitic stainless steels can be obtained by means of high-pressure metallurgy. Nitrogen content of martensitic stainless steels can also be increased by exposition of austenite to high purity nitrogen, under relatively low pressures². This can be done with bulk (case hardening) or particulate materials (powder metallurgy)³.

The beneficial effects of nitrogen on mechanical, corrosion and corrosion-erosion properties can only be obtained if nitrogen remains in solid solution after quenching or is precipitated as coherent and fine chromium nitride particles after tempering. If coarse nitride precipitation is not hindered during high temperature nitriding, chromium and nitrogen depletion of the matrix can impair corrosion and wear resistance of these steels⁴.

When stainless steel is exposed to a nitrogen atmosphere at high temperature, nitrogen may be incorporated in steel through dissolution of nitrogen in the austenitic phase up to

its solubility limit, according to equation (1):



and through precipitation of chromium nitrides, according to equations (2) and (3):



Each of these reactions has its own equilibrium constant, for given temperatures and nitrogen gas pressures.

$$K_N = \frac{h_{[N]}}{\sqrt{a_{N_2}}} = \frac{f_N \cdot [\%N]}{\sqrt{p_{N_2}}} \quad (4)$$

where $h_{[N]}$ is the Henryan activity of nitrogen in solution in austenite a_{N_2} is the Raoultian activity of nitrogen in the gas phase, which can be represented by the nitrogen partial pressure p_{N_2} . The activity activity coefficient f_N relates the

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chemical activity of nitrogen with its weight percent concentration [%N]. This relationship leads to Sieverts' law under the domain of validity of Henry's law.

$$[\%N] \approx K'' \sqrt{p_{N_2}} \quad (5)$$

where $K'' = K_N / f_N$.

Nitrogen will remain in solid solution depending on temperature of thermo-chemical treatment and nitrogen pressure. Nitrogen loss or nitrogen pickup may occur according to Sieverts' law at a given set of temperature and nitrogen partial pressure parameters.

The equilibrium of the reaction $\frac{1}{2} N_2 (\text{gas}) \leftrightarrow [N] \gamma$ may be shifted by reactions (2) and (3) relative to CrN and Cr_2N precipitation with equilibrium constants given by eqs. 6 and 7:

$$K_{CrN} = \frac{a_{CrN}}{h_{[Cr]} \cdot h_{[N]}} \quad (6)$$

$$K_{Cr_2N} = \frac{a_{Cr_2N}}{h_{[Cr]}^2 \cdot h_{[N]}} \quad (7)$$

where a_{CrN} and a_{Cr_2N} are the activities of the two chromium

nitrides and $h_{[Cr]}$ and $h_{[N]}$ are the Henryan activities of chromium and nitrogen in solution.

Extensive thermodynamic calculations must be carried out to know the nitrogen content in solution in austenite and the amount of precipitated chromium nitrides.

Thermocalc^{®5} calculations may also be done leading to a good description of the equilibrium between nitrogen gas and steel, provided that convenient databases are selected.

Nitrogen contents calculated by this procedure were compared with measured ones after high temperature nitriding of low carbon stainless steels.

2. Experimental

Fe-Cr-N phase diagrams were computed using the Thermocalc[®] (version L) program for a system in which equilibrium between austenite, 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.

Usually the equilibrium between nitrogen gas and steel is described by overlaying N_2 isobar lines⁶ on phase diagrams calculated without considering the gas phase as an equilibrium one, as shown in Fig. 1a, for Fe-13 %Cr-N alloys. It has the advantage of representing phase diagrams for different pressures all in one.

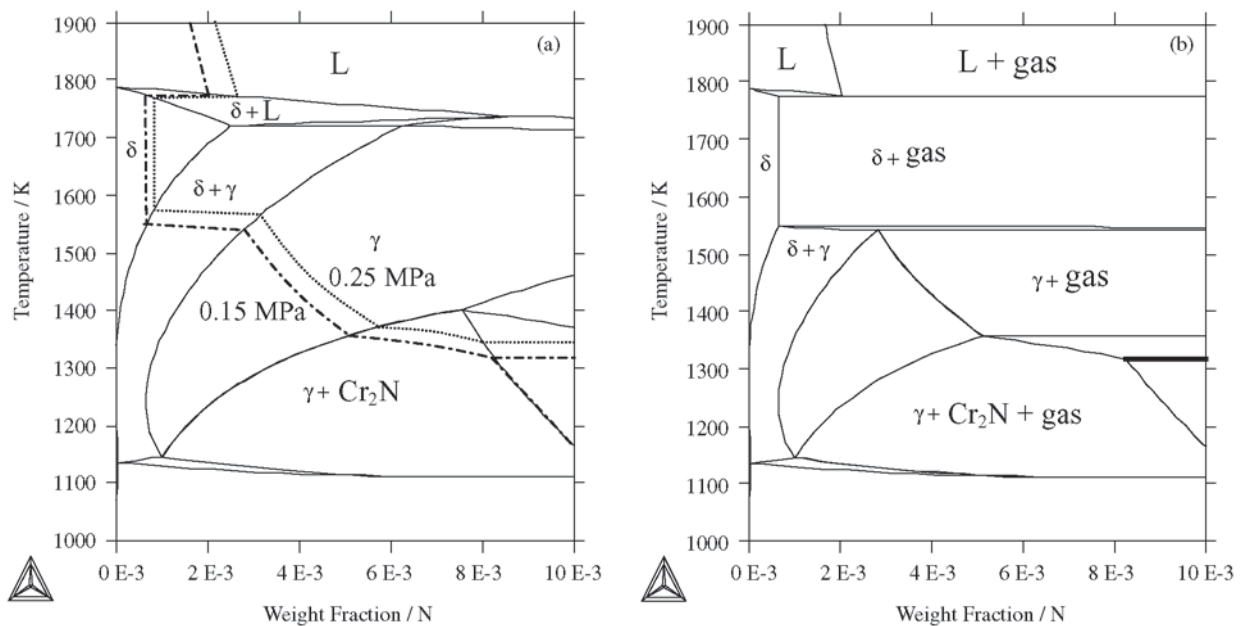


Figure 1. Fe – 13% Cr – N isopleths a) not considering the gas phase as an equilibrium one, with N_2 isobars overlaid; b) considering the N_2 gas phase as an equilibrium one.

The method used in this work considers the equilibrium between the gas phase and the steel as shown in Fig. 1b, calculated for a Fe-13%Cr-N alloy at 0.15 MPa. It gives a realistic representation of the phase fields beyond the solid state.

AISI 410S and AISI 434L stainless steels were high temperature nitrided in a tubular furnace under high purity N₂ atmosphere at pressures between 0.15 and 0.36 MPa and temperatures between 1273 K and 1473 K, during 1 to 24 h.

The AISI 410S bulk specimens were thermo-chemically treated in order to obtain hardened cases 0.15 to 2 mm thick. The AISI 434L stainless steel powder was compacted and simultaneously sintered and nitrided to obtain homogeneous and dense high nitrogen, high hardness martensitic stainless steels. The chemical compositions of the alloys are shown in Table 1.

Thermo-chemical treatments were performed at temperatures between 1273 K and 1473 K and pressures between 0.15 and 0.36 MPa, during 1 to 24 h.

Nitrogen absorbed during thermo-chemical treatment

was evaluated by measuring the increase in weight of the specimens and also by fusion under inert gas analysis to check the results. The nitrogen content at the surface of the case hardened AISI 410S steel was determined by GDOS.

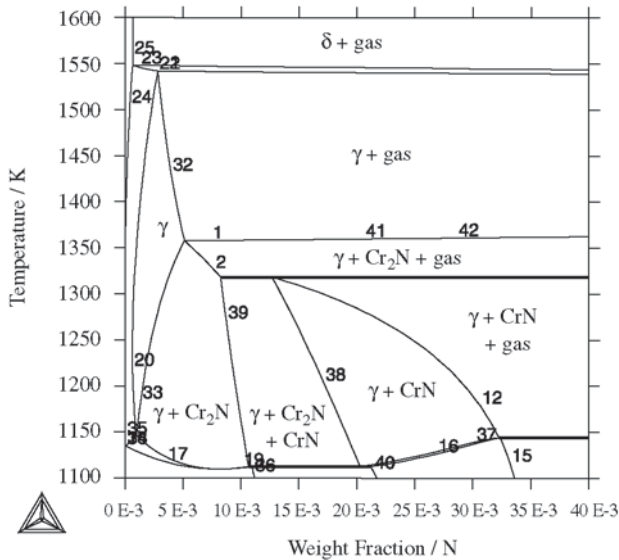
3. Results

The Fe – 13% Cr – N system and AISI 410 S alloy

Figures 2 and 3 shows isopleths of the Fe-13% Cr-N system for 0.15 MPa and 0.25 MPa. These diagrams allow predicting that, when exposed to a N₂ atmosphere, a Fe-

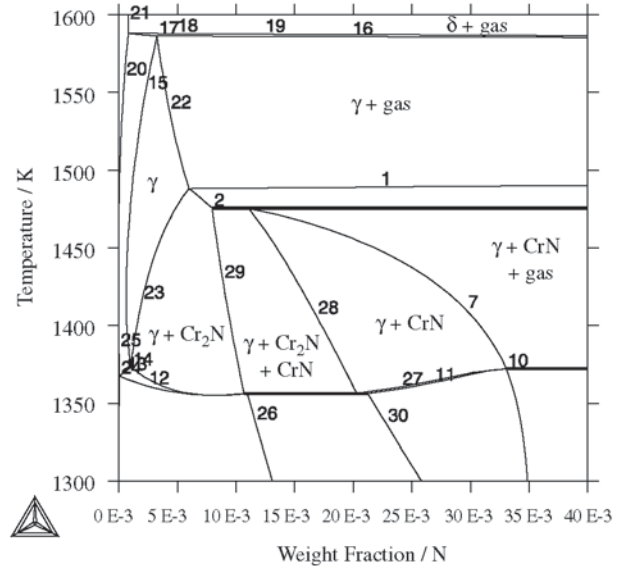
Table 1. Chemical composition of the alloys (wt.%).

Steel	C	N	Cr	Mn	Si	Mo
410 S bulk	0.07	0.020	13.0	0.27	0.40	-
434 L powder	0.02	0.018	16.2	0.20	1.20	0.8



- 1:*HCP_A3#2 GAS FCC_A1
- 2:*GAS FCC_A1 HCP_A3#2
- 12:*GAS FCC_A2 FCC_A1#2
- 15:*GAS BCC_A2 FCC_A1#2
- 16:*FCC_A1 BCC_A2 FCC_A1#2
- 17:*FCC_A1 BCC_A2 HCP_A3#1
- 18:*HCP_A3#2 BCC_A2 FCC_A1
- 19:*BCC_A2 FCC_A1 HCP_A3#2
- 20:*BCC_A2 FCC_A1
- 21:*BCC_A2 GAS FCC_A1
- 22:*GAS BCC_A2 FCC_A1
- 23:*FCC_A1 GAS BCC_A2
- 24:*FCC_A1 BCC_A2
- 25:*GAS BCC_A2
- 32:*GAS FCC_A1
- 33:*HCP_A3#2 FCC_A1
- 34:*HCP_A3#2 BCC_A2
- 35:*FCC_A1 BCC_A2
- 36:*FCC_A1#2 BCC_A2 HCP_A3#2
- 39:*FCC_A1#2 FCC_A1 HCP_A3#2
- 40:*HCP_A3#2 BCC_A2 FCC_A1#2
- 41:*HCP_A3#2 GAS FCC_A1
- 42:*HCP_A3#2 GAS FCC_A1

Figure 2. Isoleth of the Fe- 13% Cr – N system for 0.15 MPa N₂ pressure.



- 1:*HCP_A3#2 GAS FCC_A1
- 2:*GAS FCC_A1 HCP_A3#2
- 7:*GAS FCC_A1 FCC_A1#2
- 10:*GAS BCC_A2 FCC_A1#2
- 11:*FCC_A1 BCC_A2 FCC_A1#2
- 12:*FCC_A1 BCC_A2 HCP_A3#2
- 13:*HCP_A3#2 BCC_A2 FCC_A1
- 14:*BCC_A2 FCC_A1 HCP_A3#2
- 15:*BCC_A2 FCC_A1
- 16:*BCC_A2 GAS FCC_A1
- 17:*GAS BCC_A2 FCC_A1
- 18:*FCC_A1 GAS BCC_A2
- 19:*FCC_A1 GAS BCC_A2
- 20:*FCC_A1 BCC_A2
- 21:*GAS BCC_A2
- 22:*GAS FCC_A1
- 23:*HCP_A3#2 FCC_A1
- 24:*HCP_A3#2 BCC_A2
- 25:*FCC_A1 BCC_A2
- 26:*FCC_A1#2 BCC_A2 HCP_A3#2
- 27:*BCC_A2 FCC_A1 FCC_A1#2
- 28:*HCP_A3#2 FCC_A1 FCC_A1#2
- 29:*FCC_A1#2 FCC_A1 HCP_A3#2
- 30:*HCP_A3#2 BCC_A2 FCC_A1#2

Figure 3. Isoleth of the Fe- 13% Cr – N system for 0.25 MPa N₂ pressure.

13% Cr alloy absorbs larger amounts of nitrogen, the lower the temperatures, provided equilibrium is attained. Nevertheless, the amount of nitrogen in solution in austenite increases as the temperature is decreased until the Cr_2N hexagonal nitride becomes stable. From this point on the solubility limit of nitrogen in austenite decreases with decreasing temperatures. Tables 2 and 3 show for Fe –13% Cr alloys, the total nitrogen content, the nitrogen content dissolved in austenite and the phases in equilibrium with N_2 gas for different temperatures and 0.15 and 0.25 MPa pressures, respectively.

It can be seen that thermo-chemical treatments carried out at 1273 K lead to extremely high values of nitrogen absorbed by the alloy, although the nitrogen content dissolved in austenite is low and cubic CrN nitride is present. As the temperature is increased to 1373 K the total amount of nitrogen is decreased but the content of nitrogen dissolved in austenite increases. Increasing pressure stabilizes the Cr_2N phase at expenses of the cubic CrN phase.

Figure 4 shows the Fe 13% Cr – N isopleth for 0.20 MPa N_2 pressure. The small square plotted in the figure indicates the GDOS measured surface nitrogen content (1.2%) of an AISI 410 S stainless steel after 24 h of exposition to a 0.20 MPa N_2 atmosphere at 1323 K. The volume fraction of precipitated CrN at the surface of the alloy was estimated by quantitative metallography as being 3%, leading to a calculated (through mass balance) nitrogen content dissolved in austenite of 0.45%. One can see that the agreement between predicted and measured values is rather good.

Table 2. Nitrogen absorbed, nitrogen dissolved in austenite and phases in equilibrium with N_2 gas in a Fe- 13 %Cr alloy and 0.15 MPa.

Temperature (K)	% N_{total}	% N_γ	Phases in equilibrium with N_2 gas
1,273	2.30	0.25	$\gamma + \text{CrN}$
1,373	0.49	0.49	γ
1,473	0.35	0.35	γ

Table 3. Nitrogen absorbed, nitrogen dissolved in austenite and phases in equilibrium with N_2 gas in a Fe- 13 %Cr alloy and 0.25 MPa.

Temperature (K)	% N_{total}	% N_γ	Phases in equilibrium with N_2 gas
1,273	2.6	0.28	$\gamma + \text{CrN}$
1,373	0.70	0.55	$\gamma + \text{Cr}_2\text{N}$
1,473	0.45	0.45	γ

The Fe-16.2% Cr-N system and AISI 434L alloy

Phase diagrams for Fe-16.2 Cr – N alloys were calculated and Figs. 5, 6 and 7 show the isopleths for 0.15 MPa, 0.25 MPa and 0.36 MPa N_2 pressures, respectively. One can see that the solubility of nitrogen in austenite increases with increasing temperature until the gas phase becomes stable. From this point on an increase in temperature leads to a decrease in nitrogen solubility of austenite.

Nitrogen contents of sixteen AISI 434L green compact specimens, nitrided and sintered at different temperatures and N_2 pressures are plotted as small squares onto the isopleths. In Figs. 5, 6 and 7 the 1373 K and 1473 K results lay close to the solubility limit of nitrogen in austenite in equilibrium with the gas phase at 0.15 MPa. The lowest squares in Figs. 5 and 6 represent nitrogen contents of Fe-16.2% Cr specimens thermo-chemically treated at 1273 K during 6 h. These specimens did not reach equilibrium due to lower diffusion coefficients and insufficient time of exposure to the nitriding atmosphere.

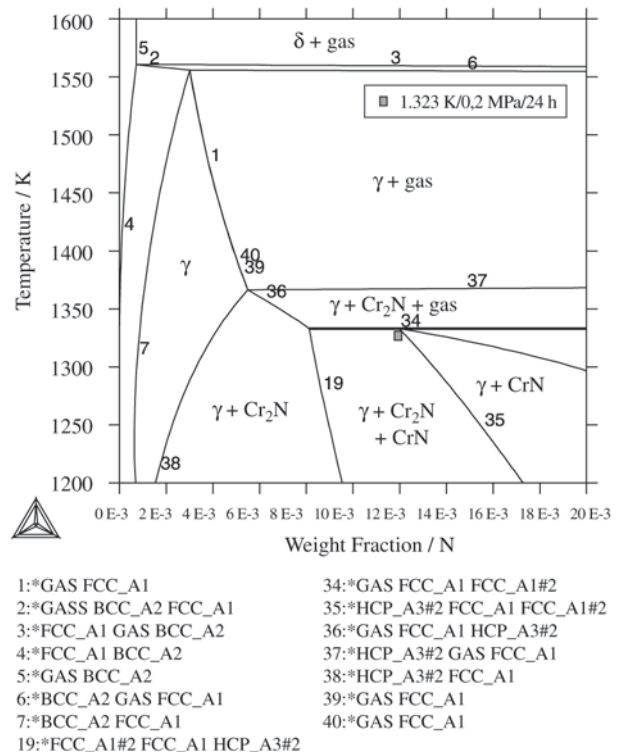


Figure 4. Isoleth of the Fe- 13% Cr – N system for 0.20 MPa N_2 pressure. The small square indicates the GDOS measured surface nitrogen content of an AISI 410 S stainless steel after 24 hours of exposure to a 0.20 MPa N_2 atmosphere at 1323 K.

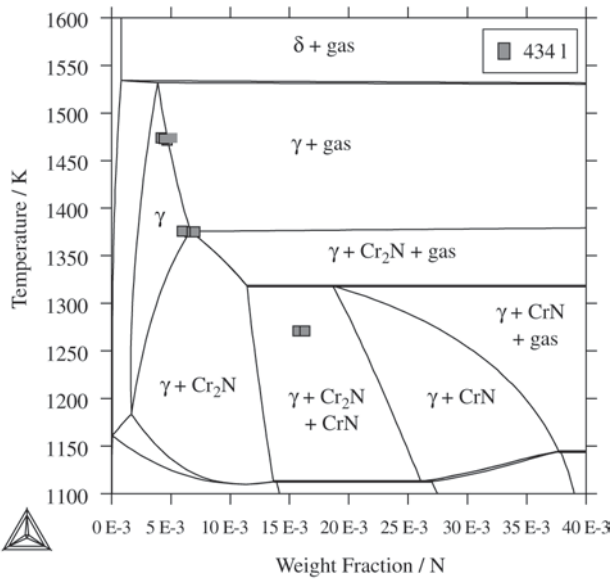


Figure 5. Isoleth of the Fe-16.2% Cr-N phase diagram and 0.15 MPa N_2 pressure. The nitrogen contents of the samples are shown as small squares.

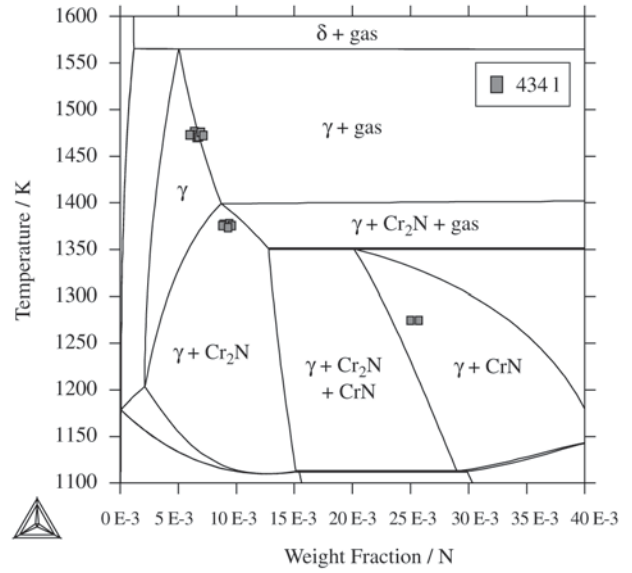


Figure 6. Isoleth of the Fe-16.2% Cr-N phase diagram and 0.25 MPa N_2 pressure. The nitrogen contents of the samples are shown as small squares.

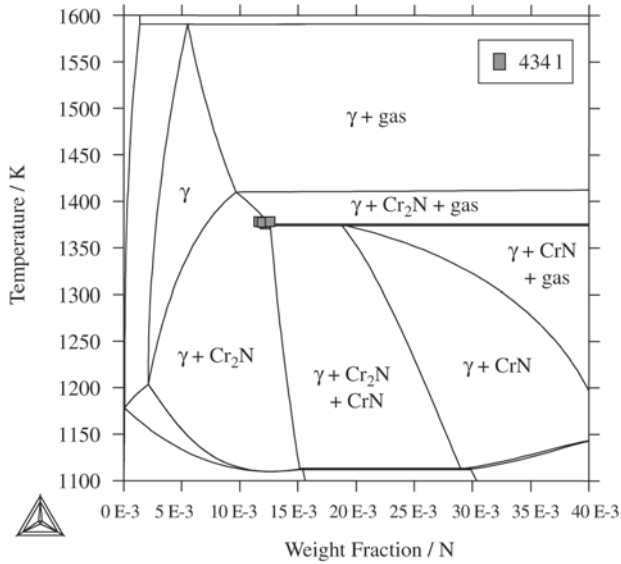
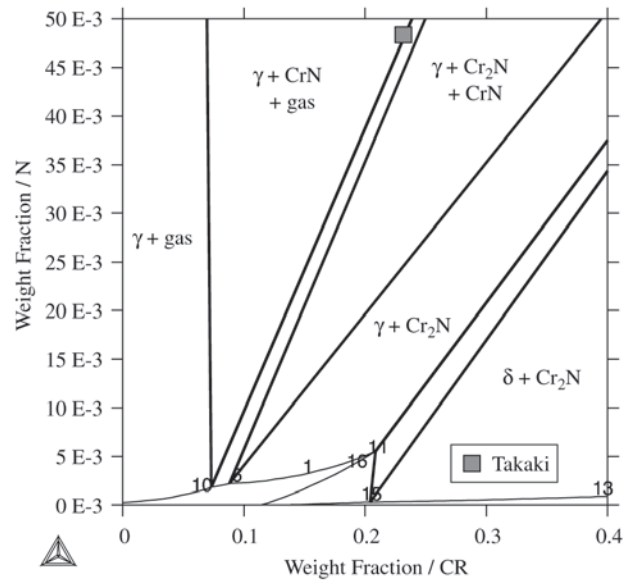


Figure 7. Isoleth of the Fe-16.2% Cr-N phase diagram and 0.36 MPa N_2 pressure. The nitrogen contents of the samples are shown as small squares.



- 1:*HCP_A3#2 FCC_A1#2
- 6:*FCC_A1 FCC_A1#2
- 10:*GAS FCC_A1#2
- 11:*HCP_A3#2 FCC_A1#2
- 13:*BCC_A2 HCP_A3#2
- 15:*BCC_A2 FCC_A1#2
- 16:*BCC_A2 FCC_A1#2

Takaki⁷ reports a total amount of 4.6 wt % N absorbed by a Fe -22% Cr alloy during a long term nitriding treatment ($t > 100$ h) at 1273 K, this value being very close to the equilibrium one indicated in the isothermal section of the Fe-Cr-N system in Fig. 8.

Figure 8. Isothermal section of the Fe-Cr-N phase diagram at 1,273 K and 0.1 MPa. The experimental results of Takaki are shown as small squares.

4. Conclusions

1. The calculated phase diagrams were in good agreement with experimental results on nitrogen absorption and nitrogen solubility in austenite obtained in high temperature nitriding experiments;
2. An appropriate choice of heat treatment parameters can lead to optimal nitrogen absorption in the alloy. Extremely high nitrogen levels can be achieved by nitrogen pickup during lower temperature treatments;
3. It was observed in the calculations that increasing pressure stabilizes CrN at expenses of Cr₂N;
4. The databases SSOL and SUB94 used in Thermocalc® version L describe thoroughly well the thermodynamics of nitrogen absorption in Fe-Cr alloys exposed to N₂ atmospheres.

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